

# Reaction Kinetics, Mechanisms and Catalysis

## EFFECT OF THE WATER-ETHANOL MOLAR RATIO IN THE ETHANOL STEAM REFORMING REACTION OVER A Co/CeO<sub>2</sub>/MgAl<sub>2</sub>O<sub>4</sub> CATALYST

--Manuscript Draft--

<b>Manuscript Number:</b>	REAC-D-14-00470
<b>Full Title:</b>	EFFECT OF THE WATER-ETHANOL MOLAR RATIO IN THE ETHANOL STEAM REFORMING REACTION OVER A Co/CeO <sub>2</sub> /MgAl <sub>2</sub> O <sub>4</sub> CATALYST
<b>Article Type:</b>	Full Paper
<b>Corresponding Author:</b>	Mariana Noelia Barroso, Ph. D. Instituto de Investigaciones en Tecnología Química San Luis, San Luis ARGENTINA
<b>Corresponding Author Secondary Information:</b>	
<b>Corresponding Author's Institution:</b>	Instituto de Investigaciones en Tecnología Química
<b>Corresponding Author's Secondary Institution:</b>	
<b>First Author:</b>	Mariana Noelia Barroso, Ph. D.
<b>First Author Secondary Information:</b>	
<b>Order of Authors:</b>	Mariana Noelia Barroso, Ph. D. Manuel F. Gomez, Ing. Luis A. Arrúa, Ph. D. María C Abello, Ph. D.
<b>Order of Authors Secondary Information:</b>	
<b>Abstract:</b>	Co(8%)/MgAl <sub>2</sub> O <sub>4</sub> catalyst with Ce addition was prepared and characterized by different techniques (BET, DRX, SEM-EDX, RTP and TG-TPO). Its catalytic performance was tested in the ethanol steam reforming reaction at 650°C and a W/FC <sub>2</sub> H <sub>5</sub> OH= 50 g min mol <sup>-1</sup> using different molar ratios H <sub>2</sub> O:C <sub>2</sub> H <sub>5</sub> OH (MR) in the feed. The presence of 5 wt.%Ce on catalyst markedly increased the hydrogen selectivity (from 3.2 to 5.2 molH <sub>2</sub> /molC <sub>2</sub> H <sub>5</sub> OH for MR=4.8) and the carbon resistance. The increase of molar ratio water:ethanol led to a significant decrease in the CO/CO <sub>2</sub> ratio (from 0.84 for RM=4.8 to 0.5 for RM=8) and in the carbon amount after 7 h in stream (from 22.9% for RM=4.8 to 6.8% for RM=8). Molar ratios higher than 7 did not significantly improved the catalytic performance. Taking into account previous studies about thermal balance of this reaction, the optimum molar ratio in the ethanol steam reforming seems to be around 6. The ethanol conversion was nearly constant after 7 h in spite of the carbon amount detected by TG-TPO and SEM-EDX. It could be inferred that an important Co fraction was exposed on the filament tips and/or a fraction of carbonaceous species was deposited on the support surface.
<b>Suggested Reviewers:</b>	Narcis Homs Universitat de Barcelona narcis.homs@qi.ub.es  Fabio B. Passos Universidade Federal Fluminense, Niterói fbpassos@vm.uff.br  Vicente Cortés Corberán I. of Catalysis and Petroleumchemistry (ICP) vcortes@icp.csic.es
<b>Opposed Reviewers:</b>	

1  
2 **EFFECT OF THE WATER-ETHANOL MOLAR RATIO IN THE ETHANOL**  
3  
4 **STEAM REFORMING REACTION OVER A Co/CeO<sub>2</sub>/MgAl<sub>2</sub>O<sub>4</sub> CATALYST**  
5  
6

7  
8  
9 **Mariana N. Barroso\*, Manuel F. Gomez, Luis A. Arrúa and Maria C. Abello**

10  
11 *Instituto de Investigaciones en Tecnología Química (INTEQUI-CONICET),*

12 *Universidad Nacional de San Luis, Facultad de Química, Bioquímica y Farmacia,*

13  
14 *Chacabuco y Pedernera, 5700 San Luis, Argentina, \*e-mail: mnbarro@unsl.edu.ar.*  
15  
16

17  
18  
19  
20  
21 **Abstract**  
22

23  
24  
25  
26 Co(8%)/MgAl<sub>2</sub>O<sub>4</sub> catalyst with Ce addition was prepared and characterized by  
27 different techniques (BET, DRX, SEM-EDX, RTP and TG-TPO). Its catalytic  
28 performance was tested in the ethanol steam reforming reaction at 650°C and a  
29 W/FC<sub>2</sub>H<sub>5</sub>OH= 50 g min mol<sup>-1</sup> using different molar ratios H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH (MR) in the  
30 feed. The presence of 5 wt.%Ce on catalyst markedly increased the hydrogen selectivity  
31 (from 3.2 to 5.2 molH<sub>2</sub>/molC<sub>2</sub>H<sub>5</sub>OH for MR=4.8) and the carbon resistance.  
32  
33

34  
35  
36  
37  
38  
39  
40  
41 The increase of molar ratio water:ethanol led to a significant decrease in the CO/CO<sub>2</sub>  
42 ratio (from 0.84 for RM=4.8 to 0.5 for RM=8) and in the carbon amount after 7 h in  
43 stream (from 22.9% for RM=4.8 to 6.8% for RM=8). Molar ratios higher than 7 did not  
44 significantly improved the catalytic performance. Taking into account previous studies  
45 about thermal balance of this reaction, the optimum molar ratio in the ethanol steam  
46 reforming seems to be around 6. The ethanol conversion was nearly constant after 7 h in  
47 spite of the carbon amount detected by TG-TPO and SEM-EDX. It could be inferred  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

1 that an important Co fraction was exposed on the filament tips and/or a fraction of  
2 carbonaceous species was deposited on the support surface.  
3  
4

5 **Keywords.** Ethanol steam reforming, hydrogen production, Co catalyst.  
6  
7  
8  
9

## 10 INTRODUCTION

11  
12  
13  
14  
15

16 As a result of increasing environmental regulations and scarcity of fossil fuels, the  
17 scientific sector has extended its research to the catalytic production of hydrogen as an  
18 energy source, particularly for its use in fuel cells [1-4]. The H<sub>2</sub> production by steam  
19 reforming of ethanol is very attractive because this alcohol is a renewable raw material  
20 which would operate in a more or less closed CO<sub>2</sub> cycle. The most studied catalysts in  
21 this reaction are those based on noble metals, Ni and Co [5-7]. Cobalt catalysts  
22 supported on a wide variety of supports have shown to be promising for the ethanol  
23 steam reforming reaction [8-11]. One problem with these catalytic systems is the high  
24 rate of deactivation related mostly to the formation of carbonaceous deposits. Among  
25 the strategies used to increase the stability of the catalyst is the addition of dopants.  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39

40 Song and Ozkan [12] have reported the effect of Ca doping on the performance of  
41 Co/CeO<sub>2</sub> catalysts in ethanol steam reforming. They found that Ca incorporation leads  
42 to the creation of oxygen vacancies and unit cell expansion in the ceria lattice. Steady  
43 state reaction studies showed a higher H<sub>2</sub> yield on Co catalysts doped with Ca. The  
44 differences in the product distribution were attributed to the ease of surface oxygen  
45 replenishment facilitated by the presence of Ca.  
46  
47  
48  
49  
50  
51  
52  
53

54 Avila-Neto et al. [13] have studied the effect of Cu addition on MgAl<sub>2</sub>O<sub>4</sub>-supported  
55 cobalt catalysts. They reported that the presence of oxidized species (Cu-O, Co-O)  
56 covering the reduced core is essential for oxidation of adsorbed carbon formed after  
57  
58  
59  
60  
61  
62  
63  
64  
65

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

activation of ethanol. They also suggested that the control of nature and composition of metal particles is an important factor determining their degree of reduction.

In a previous work, it was observed that the addition of lanthanides (Ce, Pr or La) to MgAl<sub>2</sub>O<sub>4</sub>-supported Co catalysts showed a positive effect by increasing the resistance to carbon deposition [14]. Besides, the superior performance of the catalyst promoted with 7.8 % Ce could be partially explained by the higher dispersion and reduction of Co species.

Increasing the H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH molar ratio in the feed and co-feeding oxygen to the reactor are other alternatives for controlling the carbon accumulation with time on stream. Large excesses of water affecting the overall process efficiency [15] while producing an increase in the concentration of H<sub>2</sub> and CO<sub>2</sub> and a reduction of the concentration of CO and CH<sub>4</sub> due to the methane reforming is thermodynamically promoted [16]. Low values of molar ratios may promote coke deposition on the metal sites of the catalyst, producing deactivation [15]. In literature thermodynamic studies concluded that the optimum value of H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH molar ratio for the production of H<sub>2</sub> is 3 [16], however from a study of energy integration, a high efficiency ethanol processor, including hydrogen purification and PEM fuel cell is achieved with a value between 4 and 5 [17]. Avila et al. [18] from a thermodynamic analysis of ethanol steam reforming have reported that the mole fraction of H<sub>2</sub> is not very sensitive to the H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH molar ratio between 475 and 700 °C, whereas carbon formation is highly dependent on this variable at this temperature range. Besides, the maximum mole fraction of CO<sub>2</sub> is achieved between 550 and 700°C for all H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH molar ratio. This maximum was justified by the consumption of CO and H<sub>2</sub>O by the water-gas shift reaction.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

In this work, a catalyst containing 8 wt% Co supported on MgAl<sub>2</sub>O<sub>4</sub> with the addition of Ce was prepared and characterized by different techniques. The catalyst was tested at 650°C in the ethanol steam reforming reaction. The influence of the molar ratio water-ethanol on the stability was examined.

## 2. EXPERIMENTAL

### 2.1. Catalyst preparation

MgAl<sub>2</sub>O<sub>4</sub> support (MA) was prepared by the citrate method [14]. Citric acid was added to an aqueous solution that contained the stoichiometric quantities of Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and Mg(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O. An equivalent of acid per total equivalent of metals was used. The solution was stirred for 10 min and held at boiling temperature for 30 min. Then, the solution was concentrated by evaporation under vacuum in a rotavapor at 75°C until a viscous liquid was obtained. Finally, dehydration was completed by drying the sample in a vacuum oven at 100 °C for 16 h. The sample was calcined in static air from room temperature to 500 °C at a heating rate of 5° min<sup>-1</sup> and then at 700 °C for 2 h.

The addition of Co (8 wt%) and Ce (5 wt.%) into the support was sequentially carried out by wet impregnation using an aqueous solution of Co(CH<sub>3</sub>COO)<sub>2</sub>·4H<sub>2</sub>O and Ce(CH<sub>3</sub>COO)<sub>3</sub>·xH<sub>2</sub>O. The solvent was removed in a rotating evaporator at 75°C under vacuum. The sample was dried between the impregnation steps at 100°C overnight. Finally, it was calcined in air at 600°C for 3 h. The catalyst was denoted as Co/Ce/MA.

### 2.2. Catalyst characterization

All samples were characterized using different physico- chemical methods.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

*Chemical composition.* Cobalt and cerium chemical composition was performed by inductively coupled plasma- atomic emission spectroscopy (ICP) using a sequential ICP spectrometer Baird ICP 2070 (BEDFORD, USA) with a Czerny Turner monochromator (1m optical path). Alkali fusion with  $\text{KHSO}_4$  and a subsequent dissolution with HCl solution brought the sample into solution.

*BET Surface area.* BET surface area was measured using a Micromeritics Gemini V analyzer by adsorption of nitrogen at  $-196^\circ\text{C}$  on 100 mg of a sample previously degassed at  $250^\circ\text{C}$  for 16 h under flowing  $\text{N}_2$ .

*X-ray Diffraction (XRD).* Diffraction patterns of fresh and reduced samples were obtained with a RIGAKU diffractometer operated at 30 kV and 20 mA using Ni-filtered  $\text{CuK}\alpha$  radiation ( $\lambda = 0.15418\text{ nm}$ ) at a rate of  $3^\circ\text{ min}^{-1}$  from  $2\theta = 20^\circ$  to  $80^\circ$ . The powdered sample was analyzed without a previous treatment after deposition on a quartz sample holder. The identification of crystalline phases was made by matching with the JCPDS files.

*Temperature programmed reduction (TPR).* The TPR profile was recorded in a conventional TPR equipment. This apparatus consists of a gas handling system with mass flow controllers, a tubular reactor, a linear temperature programmer, a PC for data retrieval, a furnace and various cold traps. Before the run, the sample was oxidized in a  $50\text{ mL min}^{-1}$  flow of 20 vol.%  $\text{O}_2$  in He at  $300^\circ\text{C}$  for 30 min. After that, helium was admitted to remove oxygen and finally, the system was cooled to  $25^\circ\text{C}$ . The sample was subsequently contacted with a  $50\text{ mL min}^{-1}$  flow of 5 vol. %  $\text{H}_2$  in  $\text{N}_2$ , heated at a rate of  $10^\circ\text{C min}^{-1}$  from  $25^\circ\text{C}$  to a final temperature of  $700^\circ\text{C}$  and held at  $700^\circ\text{C}$  for 2 h. Hydrogen consumption was monitored by a thermal conductivity detector after removing the formed water. The hydrogen consumption was determined by calibration with  $\text{H}_2$  (5 vol%)/ $\text{N}_2$  mixture injections.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

*Thermal gravimetry (TG-TPO).* The analyses were recorded using DTG-60 Shimadzu equipment. The samples, ca. 15 mg, were placed in a Pt cell and heated from room temperature to 1000 °C at a heating rate of 10 °C min<sup>-1</sup> with an air flow of 50 mL min<sup>-1</sup>.

Carbon deposited during reaction on used catalysts was evaluated as

$$\%C = \frac{w_{\text{coke}}}{w_{\text{catalyst}}} \times 100$$

where  $w_{\text{coke}}$  is the coke mass deposited on the catalyst calculated from the weight loss measured by TGA and  $w_{\text{catalyst}}$  is the catalyst weight free of carbon remaining after the TG analysis.

*Scanning electron microscopy and energy dispersive X-ray spectroscopy (SEM-EDX).*

Scanning electron micrographs of used samples were obtained in a LEO 1450 VP. This instrument equipped with an energy dispersive X-ray microanalyzer (EDAX Genesis 2000) and a Si(Li) detector allowed the analytical electron microscopy measurements.

The samples were sputter coated with gold.

### 2.3. Catalytic test

The ethanol steam reforming reaction was carried out in a quartz tubular reactor with an internal diameter of 4 mm operated at atmospheric pressure and 650 °C. The reactor was placed in a vertical furnace with temperature control. The reaction temperature was measured with a coaxial K thermocouple placed inside the sample. The feed to the reactor was a gas mixture of ethanol, water and helium (99.999% research grade). The liquid mixture of ethanol-water was fed to an evaporator (operated at 130°C) through an isocratic pump. The gas stream flow rates were controlled by mass flowmeters. The experimental set-up has a low pressure proportional relief valve for early detection of catalytic bed plugging. The H<sub>2</sub>O: C<sub>2</sub>H<sub>5</sub>OH molar ratio in the feed was varied from 4.8 to

8 changing the water amount with a constant ethanol concentration of 7.8 mol%, Table  
1. The catalyst weight was 50 mg (0.3-0.4 mm particle size range) without dilution in an  
inert material. Before reforming experiments, the catalyst was *in situ* reduced in  
H<sub>2</sub>(5%)/N<sub>2</sub> flow at 650°C for 1 h. After a purge in He flow, the mixture with C<sub>2</sub>H<sub>5</sub>OH +  
H<sub>2</sub>O was allowed to enter into the reactor to carry out the catalytic test. The reactants  
and reaction products were analyzed on-line by gas chromatography. H<sub>2</sub>, CH<sub>4</sub>, CO<sub>2</sub> and  
H<sub>2</sub>O were separated by a 1.8 m Carbosphere (80-100 mesh) column and analyzed by TC  
detector. Nitrogen was used as an internal standard. Besides, CO was analyzed by a  
flame ionization detector after passing through a methanizer. Higher hydrocarbons and  
oxygenated products (C<sub>2</sub>H<sub>4</sub>O, C<sub>2</sub>H<sub>4</sub>+C<sub>2</sub>H<sub>6</sub>, C<sub>3</sub>H<sub>6</sub>O, C<sub>2</sub>H<sub>5</sub>OH, etc) were separated in Rt-  
U PLOT capillary column and analyzed with FID using N<sub>2</sub> as carrier gas.

Ethanol conversion ( $X_{C_2H_5OH}$ ), selectivity to carbon products ( $S_i$ ) and hydrogen yield  
( $Y_{H_2}$ ) were estimated as described elsewhere [14].

## RESULTS AND DISCUSSION

In Table 2, the most important characterization results of the Co/Ce/MA fresh catalyst are shown. The X-ray pattern revealed the presence of the MgAl<sub>2</sub>O<sub>4</sub> and Co<sub>3</sub>O<sub>4</sub> spinels and also the fluorite phase corresponding to CeO<sub>2</sub>. The presence of CoAl<sub>2</sub>O<sub>4</sub> and CoO could not be ruled out but taking into account that the support has been thermally stabilized before impregnation and the catalyst has been calcined in air, the formation of these phases if present they should be negligible. The TPR profile showed two intense peaks at 428 and 687°C assigned to the reduction of Co<sup>3+</sup>/Co<sup>2+</sup> with different interaction extent with aluminate matrix. The reduction extent measured as mol H<sub>2</sub>/mol Co clearly indicated that the cobalt species are not completely reduced at 650°C (mol H<sub>2</sub>/mol Co=0.61). These results suggest that different Co species (Co<sup>0</sup> and Co<sup>δ+</sup>) could be



1 present on the catalytic surface at the beginning of the reaction. After reduction,  
2 incipient peaks corresponding to  $\text{Co}^0$  could be inferred from XRD. The low intensity of  
3 them did not allow to identify the crystalline structure of metallic cobalt. Lin et al. [19]  
4 have reported that the addition of  $\text{CeO}_2$  to  $\text{Co}_3\text{O}_4$  stabilizes the hcp cobalt structure at  
5 reforming temperatures up to  $600^\circ\text{C}$ . These authors claim that hexagonal close-packed  
6 (hcp) cobalt possesses higher activity than face-centered cubic (fcc) cobalt.  
7

8  
9  
10  
11  
12  
13  
14 The addition of Ce to Co/MA catalyst significantly increased the hydrogen  
15 selectivity in the steam reforming of ethanol [14]. Moreover, it decreased the carbon  
16 amount deposited under reforming conditions although it is still important. Some  
17 results are shown in Table 3. In this work, the influence of  $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}$  molar ratio in  
18 carbon accumulation rates and in activity is investigated.  
19  
20  
21  
22  
23  
24  
25

26  
27 In Figure 1, the product distribution is shown for different  $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}$  molar ratios  
28 (MR). The water concentration was varied from 38% to 60% and the ethanol  
29 concentration was kept constant at 7.8 mol%. In all the cases the catalyst showed a high  
30 ethanol conversion at  $650^\circ\text{C}$  and  $W/F_{\text{C}_2\text{H}_5\text{OH}} = 50 \text{ g min mol}^{-1}$ . The main products were  
31  $\text{H}_2$ ,  $\text{CO}_2$ ,  $\text{CO}$  and lower amounts of  $\text{CH}_4$  and  $\text{C}_2\text{H}_4\text{O}$ , which were kept nearly constant  
32 during 420 min in stream. The absence of ethylene among products could be an  
33 indication that carbonaceous deposits observed (see further) via polymerization of  $\text{C}_2$  is  
34 excluded. The selectivity to  $\text{CH}_4$  was between 5 and 6 % The product distributions for  
35 MR: 7 and 8 were very similar.  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47

48  
49 The influence of MR on ethanol conversion, hydrogen yield and selectivity to  $\text{CO}_x$  is  
50 shown in Figures 2 and 3. The conversion is almost not affected probably due to the  
51 high activity of the catalyst. In literature, a maximum in ethanol conversion has been  
52 reported when the reaction was studied over Ni catalysts with a highly diluted feed  
53 (1.6% of ethanol), a MR= 5 and negligible deactivation conditions [20].  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

1 The hydrogen yield shows an increase from 5.2 to 5.9 molH<sub>2</sub>/mol C<sub>2</sub>H<sub>5</sub>OH with the  
2 increasing MR at the reaction temperature used in this work. This increase could be  
3 related to: (i) a contribution of water-gas shift reaction ( $\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2$ ) which  
4 favors the formation of CO<sub>2</sub> and H<sub>2</sub> and (ii) a higher rate velocity of gasification,  
5 according to the stoichiometric equation:  $\text{C}_{(\text{A})} + 2 \text{H}_2\text{O} \rightarrow \text{CO}_2 + 2 \text{H}_2$  being C<sub>(A)</sub>  
6 amorphous carbon ( $\Delta G_{650^\circ\text{C}}^0 = -24.5 \text{ kJ mol}^{-1}$ ). Lin et al. [19] have reported that the  
7 addition of 10wt% of Ce to Co<sub>3</sub>O<sub>4</sub> had an important promotion effect with elevated CO<sub>2</sub>  
8 production accompanied with elevated H<sub>2</sub> production. They have suggested a significant  
9 water-gas shift activity at 600°C under reforming conditions.  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21

22 The selectivity to CO<sub>2</sub> increases and selectivity to CO decreases when increasing the  
23 H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH molar ratio, Figure 3. Avila-Neto et al. [13] in the ethanol steam  
24 reforming reaction using a Co(12%)/MgAl<sub>2</sub>O<sub>4</sub> catalyst have also reported an increase in  
25 hydrogen selectivity and in the CO<sub>2</sub>/CO ratio when the H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH molar ratio  
26 increases from 3 to 12. They have suggested that increasing the molar ratio in the feed  
27 changes the Co<sup>0</sup>/Co<sup>2+</sup> ratio, the occurrence of Water Gas Shift reaction and the acidic  
28 properties of catalytic surface.  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38

39 Other important consequence of increasing MR is the improved resistance of  
40 deactivation. The amount of carbon deposited on the catalyst used with different MR  
41 was determined by TG-TPO and EDX, Table 4. In all the cases TG-TPO shows an  
42 important weight loss between 245 and 630°C which was attributed to the carbon  
43 burning [21, 22] and oxidation of metallic particles. TG results reveal a significant  
44 decrease in the %C when increasing MR. Thus, the formation of carbon decreases in a  
45 70 % when increasing the MR from 4.8 to 8 at 650°C. Besides, the burning temperature  
46 tend to decrease suggesting a lower extent of graphitization [23] and/or different  
47 structures of carbonaceous fibers (parallel or fishbone). Ros et al. have reported that the  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

1 maximum oxidation rate for parallel fiber occurs at a lower temperature [24]. The  
2 parallel fibers are characterized by a center hole and the metallic particle on the tip. The  
3  
4 accumulation rates of carbon expressed as  $\text{mg}_{\text{carbon}} \text{g}_{\text{cat}}^{-1} \text{h}^{-1}$  are near to others in literature  
5  
6 [13]. From Figure 4, the accumulation rate of carbon seems to reach a nearly constant  
7  
8 value for MR higher than 6. Taking into account these results and the previous studies  
9  
10 about the thermal balance in the ethanol steam reforming reaction [17], a molar ratio in  
11  
12 the feed around 6 could be suggested as the optimum. The feed composition affects the  
13  
14 re-oxidation of metallic Co and the transient exchange between  $\text{Co}^0$  and  $\text{Co}^{2+}$  under  
15  
16 reaction [25]. It has been reported that the  $\text{Co}^{2+}/\text{Co}^0$  ratio has an important role in the  
17  
18 catalytic deactivation [13, 26]. Passos et al. [26] have claimed that a  $\text{Co}^{2+}/\text{Co}^0$  ratio  
19  
20 around 1/3 on  $\text{Co}/\text{Al}_2\text{O}_3$  catalysts equilibrates the ethanol conversion and carbon  
21  
22 oxidation. The oxidation state of cobalt species under different water:ethanol molar  
23  
24 ratios during the ethanol steam reforming reaction is under study.  
25  
26  
27  
28  
29  
30  
31

32 The SEM micrographs of the used catalysts are shown in Figure 5. The images reveal  
33  
34 an important amount of filaments for the sample used with MR=4.8, which substantially  
35  
36 decreases when increasing MR. In spite of carbon amount, the activity is almost  
37  
38 constant. This behavior is suggesting that the metallic Co is exposed at the tip of the  
39  
40 fiber (justifying the negligible deactivation observed during more than 400 min on  
41  
42 stream). A fraction of amorphous carbon could also be deposited on the support and  
43  
44 could be removed by gasification as it was suggested above.  
45  
46  
47  
48  
49  
50  
51

## 52 CONCLUSIONS

53  
54  
55  
56

57 A  $\text{Co}(8\% \text{p/p})/\text{MgAl}_2\text{O}_4$  catalyst promoted with 5 wt.%Ce was investigated in the  
58  
59 ethanol steam reforming reaction with different  $\text{H}_2\text{O}:\text{C}_2\text{H}_5\text{OH}$  molar ratios at  $650^\circ\text{C}$ . A  
60  
61  
62  
63  
64  
65

1 decrease in the CO/CO<sub>2</sub> ratio was accompanied with a high hydrogen production  
2 suggesting a significant water gas shift activity and the occurrence of the gasification  
3 reaction. A higher H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH molar ratio increases the hydrogen production and  
4 decreases de CO amount without affecting the activity substantially.  
5  
6  
7

8  
9 The ethanol conversion was nearly constant during 7 h in time on stream although  
10 carbonaceous deposits were detected by TG-TPO and SEM-EDX. It could be inferred  
11 that an important fraction of Co<sup>0</sup> is exposed on the filament tips and /or other  
12 carbonaceous species could also be deposited on the support surface and removed by  
13 gasification. The accumulation carbon rate and the amount of filaments clearly  
14 decreased when increasing H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH molar ratio from MR=4.8 to 8. The observed  
15 improvements for values higher than 6 were less significant. Taking into account these  
16 results and previous studies about the thermal balance in ethanol steam reforming, a  
17 molar ratio in the feed around 6 could be suggested as the optimum.  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30

### 31 **Acknowledgments**

32 Financial supports are acknowledged to CONICET, ANPCyT and Universidad  
33 Nacional de San Luis.  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

## References

- [1] Midilli A, Ay M, Dincer I, Rosen MA (2005) On hydrogen and hydrogen energy strategies: I: current status and needs. *Renew Sust Energy Rev* 9: 255-271.
- [2] Barreto L, Makihiro A, Riahi K (2003) The hydrogen economy in the 21st century: a sustainable development scenario. *Int J Hydrogen Energy* 28:267-284.
- [3] Balat M, Balat M (2009) Political, economic and environmental impacts of biomass-based hydrogen. *Int J Hydrogen Energy* 34:3589-3603.
- [4] Ni M, Leung DY, Leung MKH (2007) A review on reforming bio-ethanol for hydrogen production. *Int J Hydrogen Energy* 32:3238-3247.
- [5] Liguras DK, Kondarides DI, Verykios XE (2003) Production of hydrogen for fuel cells by steam reforming of ethanol over supported noble metal catalysts. *Appl Catal B* 43:345-354.
- [6] Breen JP, Burch R, Coleman HM (2002) Metal-catalysed steam reforming of ethanol in the production of hydrogen for fuel cell applications. *Appl Catal B* 39: 65-74.
- [7] Busca G, Costantino U, Montanari T, Ramis G, Resini C, Sisani M (2010) Nickel versus cobalt catalysts for hydrogen production by ethanol steam reforming: Ni-Co-Zn-Al catalysts from hydrotalcite-like precursors. *Int J Hydrogen Energy* 35:5356-5366.
- [8] Batista M, Santos R, Assaf E, Assaf J, Ticianelli E (2003) Characterization of the activity and stability of supported cobalt catalysts for the steam reforming of ethanol. *J Power Sources* 124:99-103.
- [9] Llorca J, Homs N, Sales J, de la Piscina P (2002) Efficient production of hydrogen over supported cobalt catalysts from ethanol steam reforming. *J Catal* 209:306-317.
- [10] Soykal I, Bayram B, Sohn H, Gawade P, Miller JT, Ozkan U (2012) Ethanol steam reforming over Co/CeO<sub>2</sub> catalysts: Investigation of the effect of ceria morphology. *Appl Catal A* 449: 47-58.
- [11] Barroso MN, Gomez M, Arrua L, Abello M C (2010) CoZnAl catalysts for ethanol steam reforming reaction. *Chem Eng J* 158:225-232.
- [12] Song H, Ozkan U (2010) Changing the oxygen mobility in Co/Ceria catalysts by Ca incorporation: Implications for ethanol steam reforming. *J Phys Chem A* 114:3796-3801.
- [13] Avila-Neto C N, Zanchet D, Hori CE, Ribeiro RU, Bueno JMC (2013) Interplay between particle size, composition, and structure of MgAl<sub>2</sub>O<sub>4</sub>-supported Co-Cu

1 catalysts and their influence on carbon accumulation during steam reforming of ethanol.  
2 J Catal 307:222-237.

3 [14] Barroso MN, Gomez MF, Arrua LA, Abello MC (2014) Co catalysts modified by  
4 rare earths (La, Ce or Pr) for hydrogen production from ethanol. Int J Hydrogen Energy  
5 39:8712-8719.  
6

7 [15] Benito M, Padilla R, Rodriguez L, Sanz JL, Daza L (2007) Zirconia supported  
8 catalysts for bioethanol steam reforming: Effect of active phase and zirconia structure. J  
9 Power Sources 169:167-176.  
10

11 [16] Ioannides T (2001) Thermodynamic analysis of ethanol processors for fuel cell  
12 applications. J Power Sources 92:17-25.  
13

14 [17] Francesconi JA, Mussati MC, Mato RO, Aguirre PA (2007) Analysis of the energy  
15 efficiency of an integrated ethanol processor for PEM fuel cell systems. J Power  
16 Sources 167:151-161.  
17

18 [18] Avila CN, Hori CE, de Assis AJ (2011) Thermodynamic assessment of hydrogen  
19 production and cobalt oxidation susceptibility under ethanol reforming. Energy  
20 36:4385-4395.  
21

22 [19] Lin SS-Y, Kim DH, Ha SY (2009) Metallic phases of cobalt-based catalysts in  
23 ethanol steam reforming: The effect of cerium oxide. Appl Catal A 355:69-77.  
24

25 [20] Mas V, Baronetti G, Amadeo N, Laborde MA (2008) Ethanol steam reforming  
26 using Ni(II)-Al(III) layered double hydroxide as catalyst precursor: Kinetic study. Chem  
27 Eng J 138:602-607.  
28

29 [21] Guo J, Lou H, Zhao H, Chai D, Zheng X (2004) Dry reforming of methane over  
30 nickel catalysts supported on magnesium aluminate spinels. Appl Catal A 273:75-82.  
31

32 [22] Nandini A, Pant K, Dhingra S (2005) K-, CeO<sub>2</sub>-, and Mn-promoted Ni/Al<sub>2</sub>O<sub>3</sub>  
33 catalysts for stable CO<sub>2</sub> reforming of methane Appl Catal A 290:166-174.  
34

35 [23] Sánchez-Sánchez M, Navarro R M, Fierro JLG (2007) Ethanol steam reforming  
36 over Ni/M<sub>x</sub>O<sub>y</sub>-Al<sub>2</sub>O<sub>3</sub> (M=Ce, La, Zr and Mg) catalysts: Influence of support on the  
37 hydrogen production. Int J Hydrogen Energy 32:1462-1471.  
38

39 [24] Ros T, Van Dillen A, Geus J, Koningsberger D (2002) Surface oxidation of carbon  
40 nanofibres. Chem Eur J 8:1151-1162.  
41

42 [25] Lin SS-Y, Kim DH, Engelhard MH, Ha SY (2010) Water-induced formation of  
43 cobalt oxides over supported cobalt/ceria-zirconia catalysts under ethanol-steam  
44 conditions. J Catal 273:229-235.  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

[26] Passos A, Martins L, Pulcinelli S, Santilli C, Briois V (2014) Effect of the balance between Co(II) and Co(0) oxidation states on the catalytic activity of cobalt catalysts for Ethanol Steam Reforming. Catal Today 229:88-94.

1  
2  
3  
4  
5  
6  
7  
8  
9  
10  
11  
12  
13  
14  
15  
16  
17  
18  
19  
20  
21  
22  
23  
24  
25  
26  
27  
28  
29  
30  
31  
32  
33  
34  
35  
36  
37  
38  
39  
40  
41  
42  
43  
44  
45  
46  
47  
48  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65

1 **FIGURE CAPTIONS**

2  
3  
4  
5  
6 **Figure 1.** Product distribution in the ethanol steam reforming reaction over Co/Ce/MA  
7 catalyst at 650 °C,  $W/F_{C_2H_5OH} = 50 \text{ g min mol}^{-1}$ , initial ethanol concentration= 7.8 mol  
8 %, atmospheric pressure and different  $H_2O/C_2H_5OH$  molar ratios (MR). ●:  $CO_2$ , ▼:  
9 CO, ★:  $CH_4$ , ■:  $C_2H_4O$ , ○: mol  $H_2$ /mol  $C_2H_5OH$ .  
10  
11  
12  
13  
14  
15  
16  
17

18 **Figure 2.** Effect of  $H_2O/ C_2H_5OH$  molar ratio on ethanol conversion, ◆, and hydrogen  
19 yield, ○. Reaction temperature: 650 °C,  $W/F_{C_2H_5OH} = 50 \text{ g min mol}^{-1}$ , initial ethanol  
20 concentration= 7.8 mol % and atmospheric pressure.  
21  
22  
23  
24  
25  
26

27 **Figure 3.** Effect of  $H_2O/ C_2H_5OH$  molar ratio on selectivity to CO, ▼, and  $CO_2$ , ●.  
28 Reaction temperature= 650 °C,  $W/F_{C_2H_5OH} = 50 \text{ g min mol}^{-1}$ , initial ethanol  
29 concentration= 7.8 mol % and atmospheric pressure.  
30  
31  
32  
33  
34  
35  
36

37 **Figure 4:** Accumulation rate of carbon under ethanol steam reforming as a function of  
38  $H_2O/ C_2H_5OH$  molar ratio. Reaction temperature= 650 °C,  $W/F_{C_2H_5OH} = 50 \text{ g min mol}^{-1}$ ,  
39 initial ethanol concentration= 7.8 mol % and atmospheric pressure.  
40  
41  
42  
43  
44  
45  
46

47 **Figure 5.** SEM images of Co/Ce/MA catalyst used in ethanol steam reforming at  
48 different  $H_2O/C_2H_5OH$  molar ratios: MR= a) 4.8, b) 6, c) 7 and d) 8.  
49  
50  
51  
52  
53  
54  
55  
56  
57  
58  
59  
60  
61  
62  
63  
64  
65



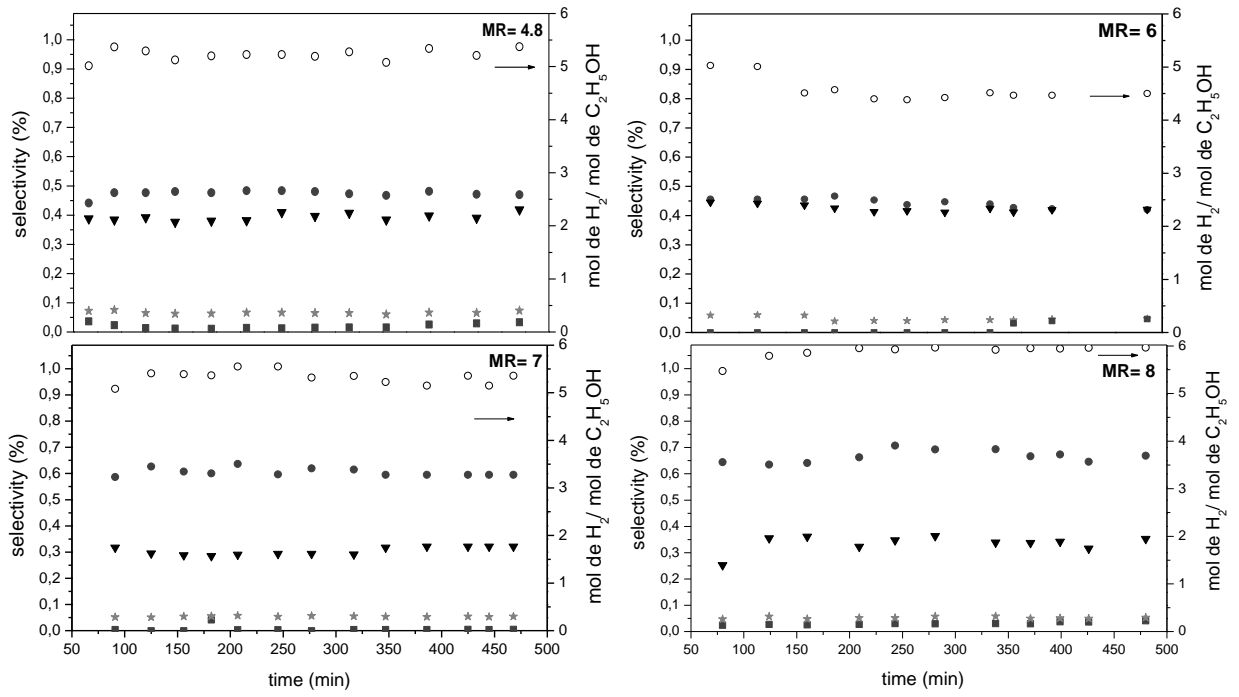


Figure 1

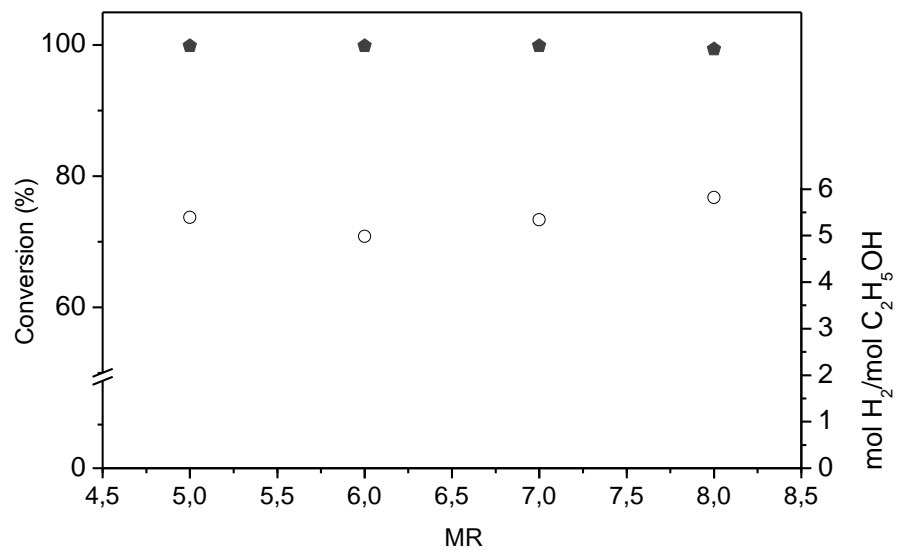
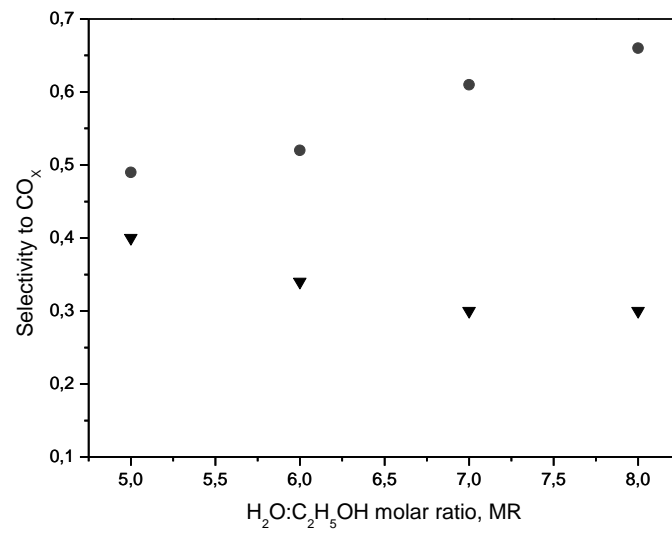
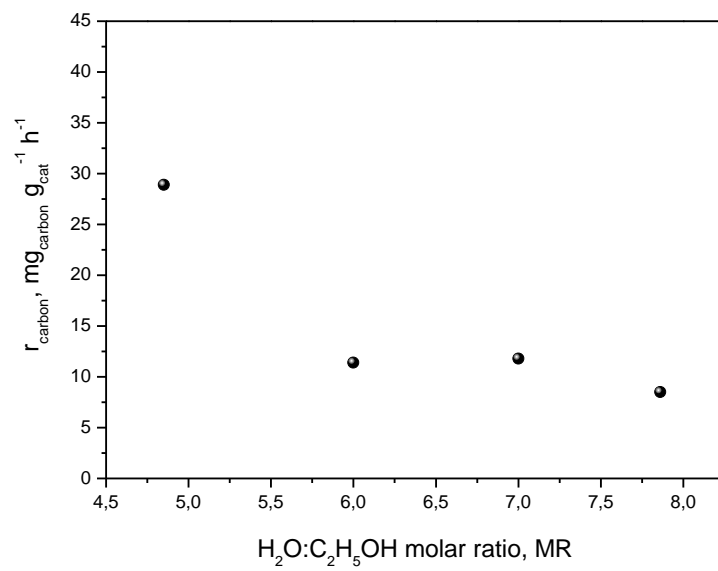


Figure 2



**Figure 3**



**Figure 4**

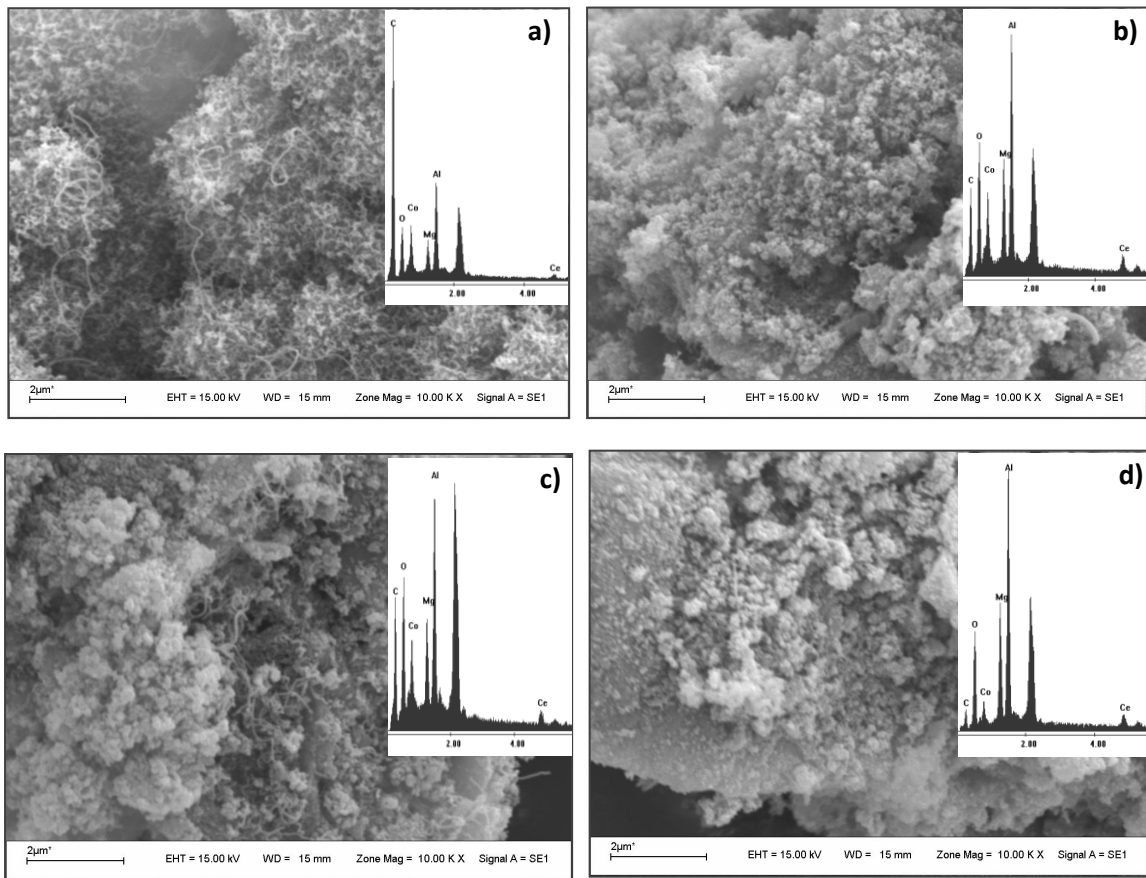


Figure 5

**Table 1.** Initial feed conditions

MR H <sub>2</sub> O/C <sub>2</sub> H <sub>5</sub> OH mol/mol	H <sub>2</sub> O mol %	C <sub>2</sub> H <sub>5</sub> OH mol %	W/F <sub>C<sub>2</sub>H<sub>5</sub>OH</sub> g min mol <sup>-1</sup>
4.85	37.86	7.81	49.0
6.00	46.75	7.79	49.8
7.00	54.55	7.79	50.4
7.86	60.14	7.65	51.2

**Table 2.** Characteristics of Co/Ce/MA fresh catalyst

S <sub>PBET</sub> g m <sup>-2</sup>	Chemical composition, wt.%		XRD Phases	TPR Result Temperature, °C	
	Co	Ce		1 <sup>st</sup> Peak	2 <sup>nd</sup> Peak
73.6	6.5	7.8	MgAl <sub>2</sub> O <sub>4</sub> , Co <sub>3</sub> O <sub>4</sub> , CeO <sub>2</sub>	428 Co <sup>3+</sup> /Co <sup>2+</sup>	687 Co <sup>δ+</sup>

Nominal loading: 8.0 wt% Co and 5.0 wt.% Ce

Co<sup>δ+</sup>: Co species strongly interacting with MgAl<sub>2</sub>O<sub>4</sub>.

**Table 3.** Catalytic results in the ethanol steam reforming over Co/MA with and without Ce addition [14]

Catalyst	X <sub>C<sub>2</sub>H<sub>5</sub>OH</sub> %	R <sub>CO/CO<sub>2</sub></sub>	S <sub>C<sub>2</sub>H<sub>4</sub>O</sub> %	mol H <sub>2</sub> /mol C <sub>2</sub> H <sub>5</sub> OH	TG-OTP	
					%C	T <sub>burned</sub> , °C
Co/MA	90	1.08	27	3.3	30.2	521
Co/Ce/MA	99.9	0.83	3	5.2	22.9	496

Reaction conditions: T= 650°C; H<sub>2</sub>O:C<sub>2</sub>H<sub>5</sub>OH molar ratio = 4.8; W/F<sub>C<sub>2</sub>H<sub>5</sub>OH</sub>= 50 g min mol<sup>-1</sup>.

**Table 4.** Amount of carbon on Co/Ce/MA catalyst after being used in reaction

MR H <sub>2</sub> O/C <sub>2</sub> H <sub>5</sub> OH	T <sub>burned</sub> , °C	%C <sub>TG-TPO</sub>	%C <sub>EDX</sub>
4.8	496	22.9	62.1
6	435	7.6	28.2
7	401	9.5	35.0
8	444	6.8	13.2

## Copyright Transfer Statement

Publisher: Akadémiai Kiadó Zrt., Budapest, Hungary

The signed Copyright Transfer Statement please return to:  
<http://www.editorialmanager.com/reac/>

### Author

Name: Mariana N. Barroso

Address: Chacabuco y Pedernera, 5700 San Luis, Argentina

E-mail address: [mnbarro@unsl.edu.ar](mailto:mnbarro@unsl.edu.ar)

### Article information

Title: EFFECT OF THE WATER-ETHANOL MOLAR RATIO IN THE ETHANOL STEAM REFORMING REACTION OVER A Co/CeO<sub>2</sub>/MgAl<sub>2</sub>O<sub>4</sub> CATALYST

Journal title: **Reaction Kinetics, Mechanisms and Catalysis**

Co-authors: Manuel F. Gomez, Luis A. Arrúa and María C. Abello

### I. Transfer of copyright

By execution of the present Statement Author transfers copyright and assigns exclusively to Publisher all rights, title and interest that Author may have (for the extent transferable) in and to the Article and any revisions or versions thereof, including but not limited to the sole right to print, publish and sell the Article worldwide in all languages and media. Transfer of the above rights is referred to as those of the final and published version of the Article but does not restrict Author to self-archive the preprint version of his/her paper (see Section III).

### II. Rights and obligations of Publisher

The Publisher's rights to the Article shall especially include, but shall not be limited to:

- ability to publish an electronic version of the Article via the website of the publisher Akadémiai Kiadó, [www.akademiai.com](http://www.akademiai.com) (in Hungary), as well as the co-publisher's website, [www.SpringerLink.com](http://www.SpringerLink.com) (outside of Hungary) or any other electronic format or means of electronic distribution provided by or through Akadémiai Kiadó or Springer from time to time, selling the Article world-wide (through subscriptions, Pay-per-View, single archive sale, etc.)
- transforming to and selling the Article through any electronic format
- publishing the Article in the printed Journals as listed on the official Website of Publisher
- transferring the copyright and the right of use of the Article onto any third party
- translating the Article
- taking measures on behalf of the Author against infringement, inappropriate use of the Article, libel or plagiarism.

Publisher agrees to send the text of the Article to the e-mail address of Author indicated in the present Statement for preview before the first publishing either in paper and/or electronic format (Proof). Author shall return the corrected text of the Article within 2 days to the Publisher. Author shall, however, not make any change to the content of the Article during the First Proof preview.

### III. Rights and obligations of Author

The Author declares and warrants that he/she is the exclusive author of the Article – or has the right to represent all co-authors of the Article (see Section IV) – and has not granted any exclusive or non-exclusive right to the Article to any third party prior to the execution of the present Statement and has the right therefore to enter into the present Statement and entitle the Publisher the use of the Article subject to the present Statement. By executing the present Statement Author confirms that the Article is free of plagiarism, and that Author has exercised reasonable care to ensure that it is accurate and, to the best of Author's knowledge, does not contain anything which is libelous, or obscene, or infringes on anyone's copyright, right of privacy, or other rights. The Author expressly acknowledges and accepts that he/she shall be entitled to no royalty (or any other fee) related to any use of the Article subject to the present Statement. The Author further accepts that he/she will not be entitled to dispose of the copyright of the final, published version of the Article or make use of this version of the Article in any manner after the execution of the present Statement. The Author is entitled, however, to self-archive the preprint version of his/her manuscript. The preprint version is the Author's manuscript or the galley proof or the Author's manuscript along with the corrections made in the course of the peer review process. The Author's right to self-archive is irrespective of the format of the preprint (.doc, .tex, .pdf) version and self-archiving includes the free circulation of this file via e-mail or publication of this preprint on the Author's webpage or on the Author's institutional repository with open or restricted access. When self-archiving a paper the Author should clearly declare that the archived file is not the final published version of the paper, he/she should quote the correct citation and enclose a link to the published paper ([http://dx.doi.org/\[DOI of the Article without brackets\]](http://dx.doi.org/[DOI of the Article without brackets])).

### IV. Use of third party content as part of the Article

When not indicating any co-authors in the present Statement Author confirms that he/she is the exclusive author of the Article. When indicating co-authors in the present Statement Author declares and warrants that all co-authors have been listed and Author has the exclusive and unlimited right to represent all the co-authors of the Article and to enter into the present Statement on their behalf and as a consequence all declarations made by Author in the present Statement are made in the name of the co-authors as well. Author also confirms that he/she shall hold Publisher harmless of all third-party claims in connection to non-authorized use of the Article by Publisher. Should Author wish to reuse material sourced from third parties such as other copyright holders, publishers, authors, etc. as part of the Article, Author bears responsibility for acquiring and clearing of the third party permissions for such use before submitting the Article to the Publisher for acceptance. Author shall hold Publisher harmless from all third party claims in connection to the unauthorized use of any material under legal protection forming a part of the Article.

### V. Other provisions

Subject to the present Statement the Article shall be deemed as first published within the Area of the Hungarian Republic. Therefore the provisions of the Hungarian law, especially the provisions of Act LXXVI of 1999 on Copy Rights shall apply to the rights of the Parties with respect to the Article. For any disputes arising from or in connection with the present Statement Parties agree in the exclusive competence of the Central District Court of Pest or the Capital Court of Budapest respectively.

Mariana N. Barroso

San Luis, 04/12/2014

Author

Signature

Date and Place



<http://www.springer.com/journal/11144>

Reaction Kinetics, Mechanisms and Catalysis

Editor-in-Chief: Fabian, I.

ISSN: 1878-5190 (print version)

ISSN: 1878-5204 (electronic version)

Journal no. 11144