

Hydrogen produced from ethanol for internal reforming molten carbonate fuel cell

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Abstract

Ethanol is proposed as alternative fuel for the indirect internal reformer of molten carbonate fuel cells (IIR-MCFCs). At MCFCs working conditions ($T = 923$ K and $P = 1$ bar), both Rh- and Co-based catalysts have been tested using diluted ethanol/water mixture. The steam/carbon ratio of the feed was selected close to 4.2 mol/mol, in the aim to simulate the composition of ethanol/water mixture produced from biomasses. A good performance on Rh-based catalysts was reached for a sample containing 5 wt.% of Rh on Al_2O_3 , while Co-based catalysts were suitable only for higher loading of active phase (i.e. 20 wt.%). The supports influence has been also investigated as well as different behavior was been found as a function of their nature. In fact, while Rh (5 wt.%) doped Al_2O_3 seems to be stable and active catalyst, the Co (20 wt.%) Al_2O_3 decays in short time because of coke deposition. The MgO represents a more suitable support for Co catalyst because of its lower acidity with respect to Al_2O_3 . Samples of Co (20 wt.%) MgO catalysts have been found more stable than Co/ Al_2O_3 (low coke formation) and reached performance levels comparable to that of Rh/ Al_2O_3 . Although Co/ MgO required higher contact times than Rh/ Al_2O_3 , to be used in IIR-MCFCs, it represents an interesting and cheaper alternative to noble metal (Rh). © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Steam reforming; Hydrogen production; Molten carbonate fuel cell; Cobalt; Rhodium; Ethanol

1. Introduction

The massive use of fuels derived from crude oil is a key factor in the environmental pollution problems and the world looks with increasing interests to enforce research activities on the development of alternative fuels. In this aim, one of the most interesting by-products of corn is the ethanol that can be easily produced by fermentation of the starch contained in it. Researches on genetic modification have been addressed to the development of corn plants more resistant to sickness and yeast that can convert greater percentage of starch to ethanol. It could allow the production of ethanol at lower cost with respect to the past. A further reduction of the cost of the energy produced by ethanol oxidation could be obtained by using directly the ethanol/water mixture as produced just after the fermentation and before the distillation step needed to produce concentrated ethanol. In this sense, we are studying the use of ethanol/water mixture (1/10 v/v) as fuel to supply molten carbonate fuel cells (MCFCs) in the configuration of internal reforming. The

concept of internal reforming can be achieved in MCFC through two different geometric configurations, called direct internal reforming (DIR) and indirect internal reforming (IIR). In the first one DIR, the reforming catalyst will be placed inside the gas anodic compartment, and thus, the produced hydrogen will be immediately oxidized by the anode electrochemical cell reaction. By this configuration, the thermodynamic equilibrium is moved towards the full conversion of the fuel to CO_2 and H_2 . Instead, in the IIR, the catalyst will be placed into anodic manifolds and there is not any physical contact with anodic compartment. The reaction is thermodynamically controlled by the involved equilibria and only the temperature is the determining parameter. In both cases, the steam reforming process is sustained by the heat rejected from the cell reactions and no heat exchangers are needed, further the process is carried out at cell temperature (i.e. $T = 923$ K). This research is aimed to the development of a molten carbonate fuel cell capable to directly convert the ethanol/water mixture to electricity and heat into the anode compartment. The critical aspect of this project concerns the development of a suitable catalyst to be placed into the cell. The main properties of this catalyst comprise: stability and high activity to ethanol

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steam reforming process at cell operative conditions, high yields to hydrogen and carbon dioxide and resistance to coke formation.

The production of hydrogen from ethanol to supply molten carbonate fuel cells has been, already, proposed in previous papers [1,2]. In particular, the authors proposed a two stage process [1], where an intermediate pre-reformer produces acetaldehyde that is processed in a second step, at high temperature, and a single step process based on the use of Rh-based catalysts. In consideration to the fact that Rh is a very expensive, we considered interesting to investigate for a cheaper alternative one. Haga et al. [3,4] recently propose the Co-supported on various oxides as catalysts for the ethanol steam reforming in a temperature range 500–800 K, but no information are reported in the literature for Rh alternative catalysts working at higher temperatures. Starting from Haga's investigation, the ethanol steam reforming reaction has been carried out at the typical MCFC working temperature ($T_r = 923$ K), on Co/Al₂O₃ and Co/MgO catalysts. The catalysts decay rate has been considered of great importance to develop and improve a high temperature process. Although, it was recently, discussed [5,6] for these catalytic systems in similar reaction environments, no evidence that the decay mechanism can be the same in MCFC condition was been found in literature. Because of that, our interest has been, also, addressed to long-term tests and to the characterization of the fresh and used catalysts, that have been compared in terms of sintering and coke formation.

2. Experimental

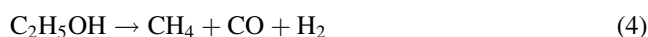
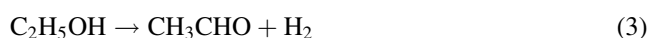
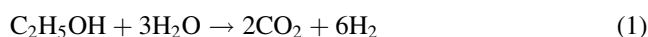
Alumina-based catalysts with different Rh and Co content were prepared by impregnating RhCl₂ or Co(N-O₃)₂·6H₂O (Aldrich) on γ -Al₂O₃ (Akzo–Nobel 001-3P), respectively. The metal content, programmed according to incipient wetness technique, was further verified by the chemical analysis of the final product. Because of the low porosity of the support (MgO–Ube #500), the Co/MgO samples were prepared by repeatedly treating the support with a concentrated solution of Co(NO₃)₂·6H₂O. After each treatment the catalyst was dried and calcined in air at 900 K. Before any treatment, the supports (Al₂O₃ or MgO) have been crushed and sieved to proper size (40–70 mesh). The physical surface area and the porosity of the supports were determined by the BET and Hg-intrusion techniques, respectively carried out with Fisons–C. Erba instruments.

Before all tests, catalysts were pre-treated at $T = 923$ K for 16 h and then reduced in situ at $T = 575$ K for 1 h under hydrogen flow ($F_{H_2} = 100$ cm³/min). Samples of treated catalysts have been analyzed by a Philips CM-12 transmission electron microscope and the measured BET surface areas were $SA_{Co/Al_2O_3} = 114.3$ m²/g, $SA_{Rh/Al_2O_3} = 107.0$ m²/g and $SA_{Co/MgO} = 37.8$ m²/g, respectively. The

endurance tests have been carried out at constant temperature ($T_r = 923$ K), while catalytic performance was previously screened by using the temperature-programmed reaction mode (TPR), where T_r was increased from 323 to 923 K, with a mean slope $dT_r/dt = 1.5$ K/min. Reagent and reacted gases have been analyzed “on line” using a Hewlett-Packard gas-chromatograph model 6890 plus following the procedures previously described [1,2]. Nitrogen (10 mol%) was used as internal standard.

The continuous flow microreactor was made by a quartz tube ($\phi_{int} = 4$ mm) packed with a catalytic bed of 2.0 cm of averaged height. The bed was formed of $\cong 0.016$ g of active catalyst pellets (40–70 mesh) diluted with SiC inert material (10 times in volume) to minimize thermal spot effects. The reagent inlet flow has been carefully controlled by an isocratic HP 1100 pump; the gas hourly space velocity (GHSV) was carefully calculated like gas flow/overall catalyst volume ratio. The ethanol/water reaction mixture, with an inlet steam/carbon molar ratio $S/C = 4.2$ mol/mol (H₂O/C₂H₅OH = 8.4 mol/mol), was vaporized at $T_v \geq 473$ K on packed SiC, where in the meantime a flow of nitrogen ($F_{N_2} = 20$ cm³/min) was added. Both nitrogen and hydrogen flows were carefully controlled using a mass flow regulator system ASM 2500.

The hydrogen yield has been evaluated by determining the molar ratio between the hydrogen produced by the reaction and the ethanol feed [$H_{2(out)}/EtOH_{(in)}$]. This calculation has been made from the stoichiometry of the following reactions:



Independently from the mechanism pathway followed by the reaction, the H₂ production can be always referred to one of the above mentioned reactions. In this manner, we are able to determine the $H_{2(out)}/EtOH_{(in)}$ ratio directly from the outlet analysis alone, by making a simple carbon balance among CO₂, CO, CH₃CHO, CH₄, C₂H₄ and unreacted C₂H₅OH.

3. Results and discussion

As reported in previous papers [7–9], when our system reaches equilibrium at $T = 923$ K, $P = 1$ bar and $S/C = 4.2$ mol/mol, each mole of ethanol produces 5.3 mol of hydrogen and the $H_{2(out)}/EtOH_{(in)} = 6$ mol/mol ratio, expected from the reaction (1) cannot never been reached. In fact, because of the equilibria (6) and (7):



Table 1
Co/Al₂O₃ activity test^a

Time on stream (h:min)	Ethanol conversion (vol.%)	Selectivity to the carbonaceous products (vol.%) (from GC analysis) ^b				
		C ₂ H ₄	CH ₃ CHO	CH ₄	CO ₂	CO
0:23	100.00	49.08	0.00	9.61	14.6	26.69
0:46	100.00	65.33	0.00	11.60	18.47	4.59
1:09	100.00	73.91	0.00	9.04	13.36	3.68
1:32	100.00	76.55	2.95	7.21	10.15	3.14
1:55	100.00	77.53	6.53	5.62	7.93	2.38
2:18	100.00	75.17	13.83	3.88	4.56	2.56
2:41	86.49	73.43	19.05	2.85	2.05	2.62
3:04	68.21	68.25	26.80	2.30	0.00	2.65
3:27	42.37	54.43	40.09	2.02	0.00	3.46
3:50	35.38	47.22	46.68	2.77	0.00	3.33
4:13	26.40	33.22	58.65	2.99	0.00	5.14
4:36	12.94	18.97	72.25	3.19	0.00	5.59
4:59	11.82	16.00	74.34	3.94	0.00	5.72

^a Experimental conditions: GHSV = 5000 h⁻¹, *T* = 923 K and *P* = 1.0 atm.

^b The coke formation on the catalyst, unreported in table, was separately determined by elementary analysis.

little amounts of methane (<2 vol.%) and some carbon monoxide (<25 vol.%) are always present in the outlet stream, also, at very high steam/carbon ratios. Our preliminary tests, carried out on the Co/Al₂O₃ catalyst, further demonstrate the presence of remarkable amount of C₂ (i.e. ethylene and acetaldehyde), intermediate in the overall reaction mechanism [2], and a lot of carbon is formed in the early reaction stage. Table 1, where results obtained from activity tests carried out on Co/Al₂O₃ catalyst are reported, clearly shows as this catalyst decays, highlighted by the decrease of the conversion, the increase of acetaldehyde and the disappearance of CO₂. Particularly, the selectivity to C₂ is mainly addressed to ethylene (ethanol dehydration product) when the catalyst is fresh (short time on stream), while dehydrogenation to acetaldehyde is favored after few hours of operations. With regard to C₁ compounds (CH₄, CO and CO₂) it has been noted that their production is secondary to the formation of C₂ and the reaction selectivity moves from CO₂ (short time on stream) to the CO production (used for several hours). Obviously, the hydrogen yields is both a function of conversion and selectivity and when mainly CO₂ is formed, the highest hydrogen yield is obtained.

The Co/Al₂O₃ decay is further enhanced with the increasing of GHSV, because the formation of coke is favored. At contrary, the Rh/Al₂O₃ and the Co/MgO catalysts seem to be very stable in the time and only a small amount of coke is formed after several hours on stream. The performance of each catalyst is reported as a function of the time on stream in Fig. 1 and as a function of GHSV in Fig. 2. As shown in Fig. 1, all catalytic systems seem to start from the same activity level, but Co/Al₂O₃ in few hours collapses because of coke deposition. The extrapolation of the curves reported in Fig. 1, help us to determine the hydrogen yields for time on stream very close to zero. At beginning of each test, the hydrogen yield is very close to the thermodynamic equilibrium value, but for Co (20 wt.)/Al₂O₃ catalyst a fast decay is detectable. Furthermore, the ethanol conversion and

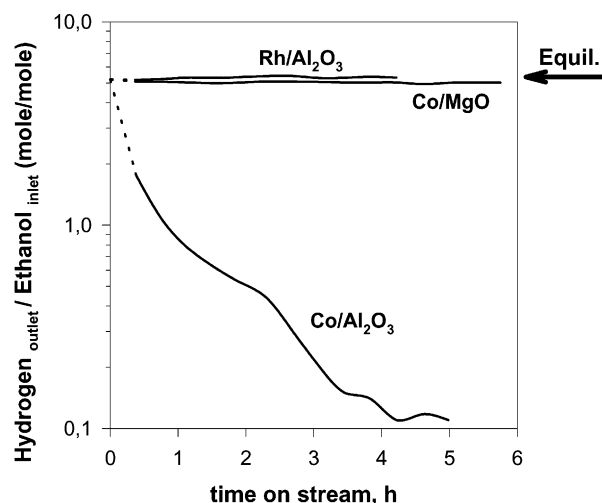


Fig. 1. Catalysts stability vs. time on stream for Rh- and Co-supported systems.

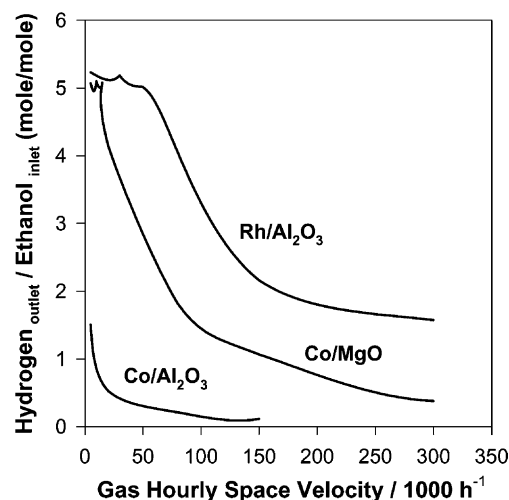


Fig. 2. The influence of GHSV on catalysts performances.

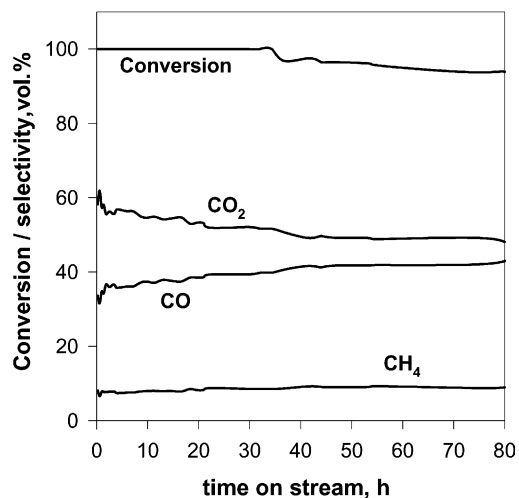


Fig. 3. Endurance test on Rh/Al₂O₃ catalyst (GHSV = 150000 h⁻¹).

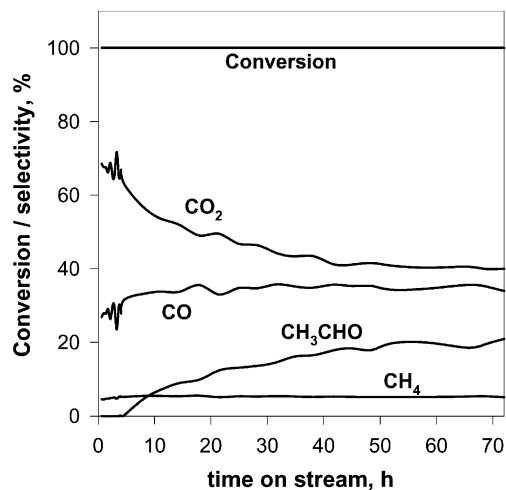


Fig. 4. Endurance test on Co/MgO catalyst (GHSV = 10000 h⁻¹).

selectivity trends are strictly dependent as a function of the time on stream. The drop off in the hydrogen production can be attributable to the incomplete transformation of the acetaldehyde into methane, carbon monoxide and carbon dioxide and/or to a lack of ethylene conversion into products

of dehydrogenation/dehydration during the first reaction steps.

As shown in Fig. 2, conditions characterized by low values of space velocity (it means high contact times) are very close to the thermodynamic equilibrium and the correspondent

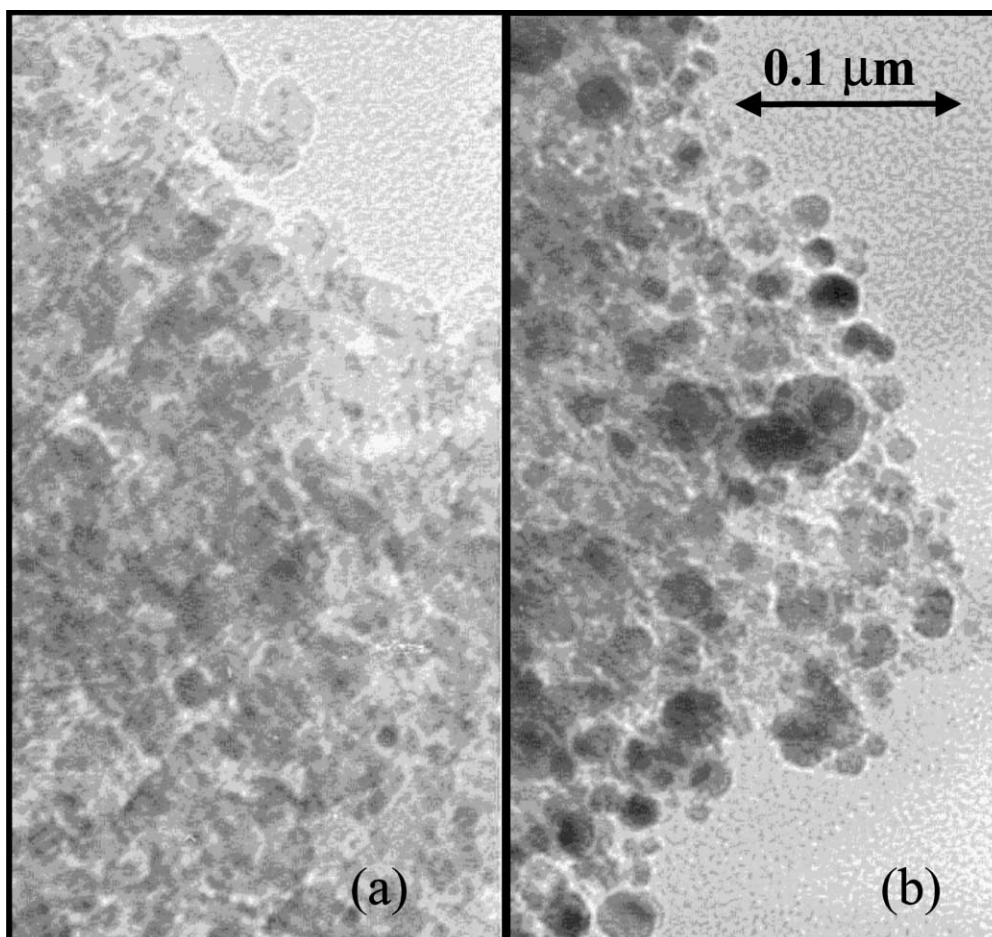


Fig. 5. TEM micrographs of the Rh/Al₂O₃ catalyst: (a) fresh; (b) after 72 h of test.

value of hydrogen yields is at the top ($H_2/EtOH > 5.0$). The hydrogen production decreases when space velocity increases and different trends depend upon the catalyst-support nature. The analysis reported in Fig. 2 are recorded after 40 min from the beginning of tests, when the catalytic systems were stabilized. Among the samples, Rh (5 wt.%)/ Al_2O_3 is the most active catalyst, while the Co (20 wt.%)/ Al_2O_3 shows the lowest activity, also if the metal loading for Co-based catalysts is four times higher than for the Rh sample. The explanation of these different activities cannot be simply related to the catalytic properties of the active phase, but is to be attributed also to the support influence. As previously reported [2], Rh is a very active metal and it acts independently from the support. The less active Co, instead, is strongly influenced by the substrates (Al_2O_3) effect that, in this case, promotes the ethanol dehydration. As well known from basic literature [10], in fact, production of ethylene precedes coke formation and this is followed by a fast deactivation. Thus, a more selective and stable Co-based catalyst can be obtained by using basic supports like MgO.

The hydrogen yields reported in Fig. 1, for the Rh/ Al_2O_3 and Co/MgO catalysts, are very constant and no meaningful variation in the ethanol conversion has been detected in few hours. To better evidence the different decay mechanisms,

the two catalysts have been compared starting from ethanol conversion and selectivity to C_1 , close to 100% (the maximum of activity), and recording the outlet analysis in long time experiments (Figs. 3 and 4, respectively). In this spite, different GHSV have been selected for Rh (5%)/ Al_2O_3 and Co (20%)/MgO (GHSV = 150 000 and 10 000 h^{-1} , respectively) because the Co is less active than Rh and at GHSV = 150 000 h^{-1} gives an ethanol conversion equal to 60% with respect to Rh (Fig. 1). As shown in Figs. 3 and 4, Rh/ Al_2O_3 catalyst produces only C_1 also at very high GHSV (conversion <100%) and time >80 h, while traces of C_2 are present on Co/MgO as soon as deactivation starts. The test on Co/MgO catalyst (Fig. 4), in fact, evidences the formation of acetaldehyde also at 100% of ethanol conversion and after few hours ($t = 5$ h) of operations, while the loss of conversion on Rh/ Al_2O_3 can be measured only after 100 h. No traces of ethylene are evident for both catalytic systems.

The reason of these different selectivities has been investigated through a microscopy characterization of the samples before and after the experiments (Figs. 5–7). Fig. 5 reports the electronic transmission micrographies (TEM) before (Fig. 5a) and after (Fig. 5b) the tests, on Rh/ Al_2O_3 catalyst. Images show that metallic micro-crystals of Rh

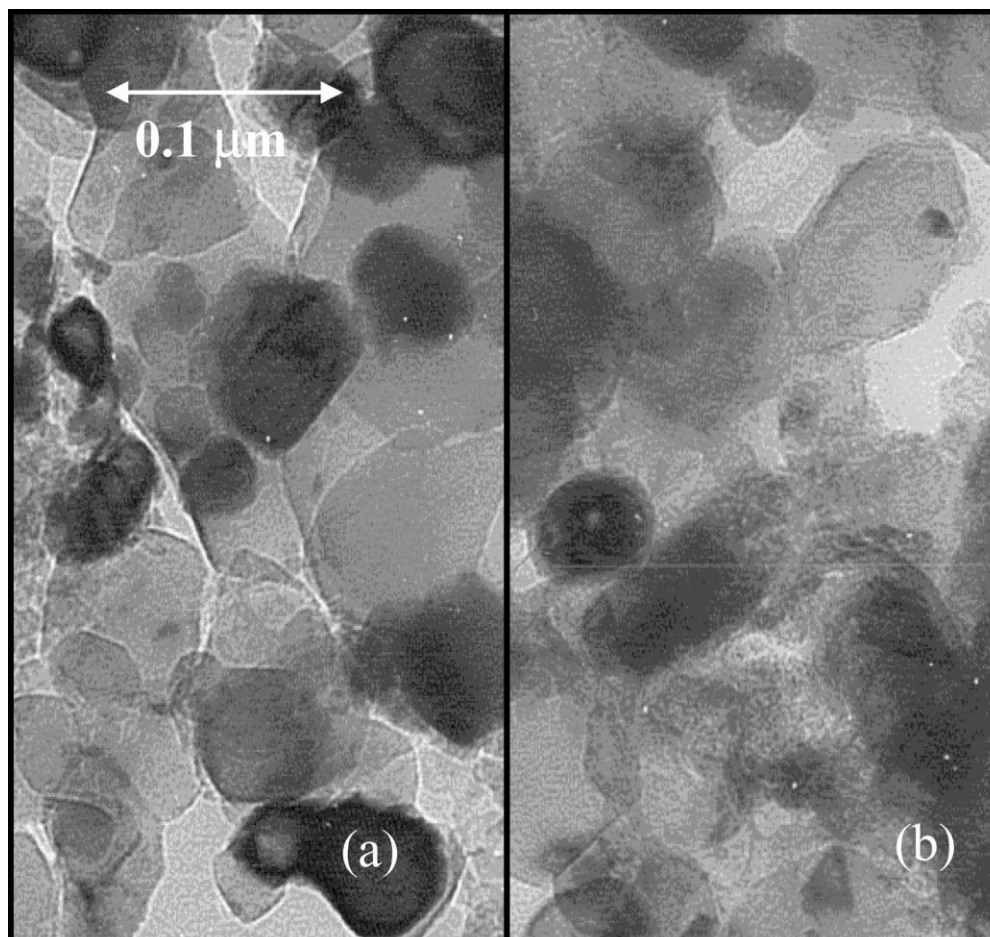


Fig. 6. TEM micrographies of the Co/MgO catalyst: (a) fresh; (b) after 72 h of test.

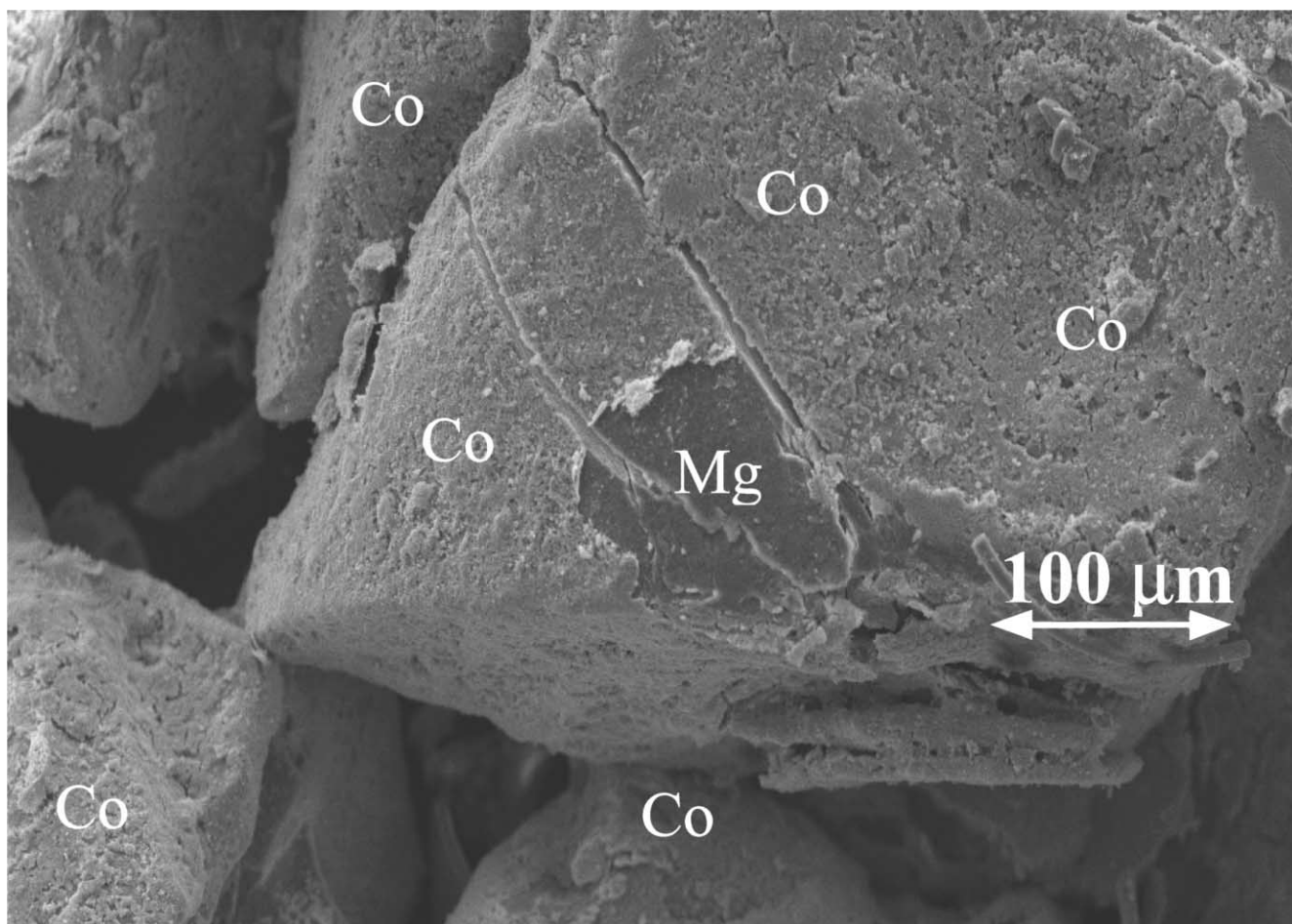


Fig. 7. SEM micrographies (180 times) and related EDX mapping of a Co/MgO fresh sample.

sinter and their averaged size (r_m) grows from 80 Å for the fresh sample, to 190 Å for the spent one. The Rh particles sintering influences the overall production of hydrogen that lowers from $H_{2(out)}/EtOH_{(in)} = 5.2$ to 4.0 mol/mol, but no change on products distribution can be detected. At the contrary, the Co/MgO catalyst (Fig. 6) starts from larger metal crystals ($r_m = 200$ Å), that grow a little with the use ($r_m = 220$ Å), and as above discussed, some acetaldehyde (~20 vol.%) can be found in the final mixture.

The low magnitude SEM photographs (180 times) and the EDX related maps on the Co/Mg system (Fig. 7), show an irregular distribution of Co on the support with a

morphology quite different to those of the Rh/Al₂O₃ and Co/Al₂O₃. In fact, as shown in Fig. 7, the elements distribution (Mg and Co) is homogeneous and a thick layer of Co is clearly evident on the external surface of MgO pellets.

The XRD spectra, made on Co-based samples (Co/Al₂O₃ and Co/MgO) before and after tests, give a further explanation about the above discussed catalytic behavior (Table 2). First of all, while in the Co/Al₂O₃ catalyst, the Co is present as a mixture of different oxides, in the Co/MgO catalyst a very large amount of metallic Co is detectable. The oxidation state of Co always increases during the time, but in the Co/MgO sample, the Co⁽⁰⁾ is the main phase also after

Table 2
XRD determinations on Co/Al₂O₃ and Co/MgO catalysts

Catalyst	Main phases	Particle size (Å)				
		Co ₂ O ₃ + Co ₃ O ₄	CoO	Al ₂ O ₃	Co	MgO
Fresh Co/Al ₂ O ₃	CoO (cubic) + Al ₂ O ₃	20	45	25	–	–
Used Co/Al ₂ O ₃ ^a	Co ₂ O ₃ + Co ₃ O ₄ (hexagonal) + Al ₂ O ₃	84	77	52	–	–
Fresh Co/MgO	Co (metallic) + MgO	–	–	–	145	338
Used Co/MgO ^a	Co + MgO + MgCo ₂ O ₄ (traces)	–	–	–	159	356

^a After 72 h of test.

several hours on stream. Taking into account that also Rh is mainly in the reduced valence state in the Rh/Al₂O₃ sample [2], we can conclude that coke formation and reaction selectivity are closely related to the oxidation state of the metal. The basicity of support plays an important role in stabilizing the Co in the metallic phase (MgO), while it does not seem to influence the Rh, always at the lowest oxidation state, because of its redox electrochemical potential. Now researches are in progress to deeper investigate the observed decay mechanism.

4. Conclusions

Ethanol steam reforming has been studied at operative conditions of a MCFC working on internal reforming mode ($T = 923$ K and $P = 1.0$ bar). Rhodium-based catalysts (i.e. Rh (5 wt.%)/Al₂O₃) show a great selectivity to C₁ compounds, also at high space velocity (GHSV up to 300 000 h⁻¹), but they are very expensive. Long-term experiments demonstrated this characteristic remains constant with the time, even if a growing of catalyst particles size can be expected. Because of Rh is a very expensive metal, our efforts have been addressed to cheaper and more available Co-based systems. A Co (20 wt.%)/Al₂O₃ catalyst has been prepared by impregnation and characterized from the catalytic and morphological points of view, both before and after each test. This catalyst evidenced a good activity toward ethanol steam reforming process, but in the meantime, the production of C₂ compound (ethylene and acetaldehyde) and coke has been recorded also after few minutes on stream. The coke formation, the sintering of metal phase and the performance decay have been investigated and a close correlation among these parameters has been stressed. A new Co-based catalysts series has been, then, prepared by a more basic support

(MgO) than alumina. No coke is formed in a short time on the catalyst surface, also if, the stability of Co (20 wt.%)/MgO seems to be lower of that of Rh (5 wt.%)/Al₂O₃. Long-term tests demonstrated this catalyst is active to fully reform ethanol, but acetaldehyde traces have been detected few hours after the start-up. Some carbon whiskers has been found on the used catalysts, and TEM micrographies seem to demonstrate that the activity loss could be correlated to “coking” rather than “sintering”. In any case, the crystallite sizes of Co are two times greater than those of Rh and SEM-EDX maps show a non homogeneous system, where the MgO support is coated by a thick Co layer. At last, a strong influence of the support on the stabilizing the metal active phase has been found by XRD and it has been observed the Co lowest oxidation state only when supported on the MgO. The coke formation is mainly correlated with the presence of no reduced CoO_x-supported on Al₂O₃.

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