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Hydrogen production by auto-thermal reforming of ethanol on Rh/Al$_2$O$_3$ catalyst

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Abstract

This study is focused to optimising a bio-ethanols auto-thermal reforming (ATR) process over 5% Rh/Al$_2$O$_3$ catalyst homemade, to produce syn-gas for fuel cell application. The effect of oxygen addition for a given S/C molar ratio ranging from 2.1 to 6.3 at $T = 923$ K was investigated, varying the O$_2$/EtOH molar ratio between 0.2 and 1.1. The results have identified an optimum range where the ethanol conversion is 100%, CH$_4$ and CO productions go down and hydrogen yield reaches a maximum before decreasing because of the prevalent oxidizing action of oxygen. The obtained data, compared with those from steam reforming (SR) process, gave a very clear indication about the potentiality of ATR process.
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Keywords: Ethanol; Hydrogen production; Auto-thermal reforming; Rhodium

1. Introduction

In the past 1930s, Lawaczek claimed the hydrogen was an innovative and cheaper method to send energy through pipelines [1]. In a wide sense, this could represent the birthday of the "*Hydrogen Economy*". Since that time, several and significant technological advances have been reached and today the hydrogen seems to be a valid candidate for a future substitution of the conventional vectors of energy. The hydrogen can be obtained from renewable sources [2,3] (like water or biomass) or from conventional hydrocarbons through thermal or catalytic processes [4,5]. In the last years, some attention has been devoted to investigate processes for the production of hydrogen and synthesis gas from bio-ethanol [6–8] through catalytic steam reforming (SR) [9–11]. A discrete interest is, also, born around the development of ethanol steam reforming processors to be coupled with fuel cells systems [12–14]. Nevertheless several attractive features are almost evident, some technological problems concern the strong endothermicity of the overall process and the development of long-term stable and coke resistant catalysts. As earlier reported [15], the auto-thermal reforming (ATR) looks a reasonable alternative process whose salient features are a reduced rate of carbon deposition and a more favourable thermal equilibrium, that can be designed as a function of the oxygen feed. Experiments carried out to measure catalytic activity of Rh based catalyst on ethanol ATR process can be also used to study other fundamental aspects of the process, like the changes of the equilibrium, the carbon deposition rate and the morphological modifications of the catalyst/support structure. In this paper we reports the results of an investigation aimed to minimize the above mentioned problems by processing bio-ethanol under auto-thermal reforming conditions that couples the exothermal oxidation with the endothermal steam reforming reactions. The results can gave interesting indications about the feasibility of this process that runs with an almost transcurable supply of external energy.

2. Experimental

2.1. Catalyst preparation and characterization

The catalyst (5% Rh/Al$_2$O$_3$), was prepared by impregnation of γ-Al$_2$O$_3$ (AKZO-NOBEL 001-3P). The impregnation was carried out with a RhCl$_2$ aqueous solution of appropriate concentration corresponding in volume to the total pore volume of the support (dry impregnation), the sample was then dried and calcined in a oven furnace

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Nomenclature

ATR	auto-thermal reforming
C_{EtOH}	ethanol conversion, $\% = (F_{in} - F_{out}/F_{in}) \times 100$
CHNS	elemental analysis of carbon, hydrogen, nitrogen and sulphur
EtOH	ethanol
F	ethanol flow (ml/min)
GHSV	gas hourly space velocity (h^{-1})
ΔH	reaction enthalpy calculated from chemical analysis (kcal/mol$_{ethanol\ converted}$), $\Delta H = (\sum_x \chi_i \Delta H_i^\circ)_{out} - (\sum_i \chi_i \Delta H_i^\circ)_{in}$
ΔH°	standard formation enthalpy (kcal/mol)
i	"i" component of the mixture
in, out	inlet or outlet composition
MAR	mass action ratio from chemical analysis MAR $= (\prod_i p_i^{n_i})_{products}/(\prod_i p_i^{n_i})_{reactants}$
MSR	methane steam reforming
$O/C = O_{2(in)}/EtOH_{(in)}$	oxygen/carbon inlet atomic ratio (mol/mol)
$S/C = H_2O_{(in)}/EtOH_{(in)}$	steam/carbon inlet molar ratio (mol/mol)
S_{H_2}	"hydrogen selectivity" from chemical analysis (mol$_{produced\ hydrogen}$/mol$_{ethanol\ converted}$)
SR	steam reforming
$S_x = \chi_x/\sum_x \chi_x$	selectivity to a carbonaceous product (x = CO, CO_2, CH_4, CH_3CHO, C_2H_4) (vol.%)
t	time on stream (h)
WGSR	water gas shift reaction
Y_{H_2}	"hydrogen yield" from chemical analysis (mol$_{produced\ hydrogen}$/mol$_{feed\ ethanol}$)

Greek symbols

τ_{EtOH}	ethanol contact time (vol$_{catal}$/F_{in}) (s)
χ	molar fraction

at 923 K for 16 h. The Rh content was determined "a posteriori" by atomic adsorption analysis. The size of the Rh crystallites (80–90 Å) was determined by transmission electron microscopy (TEM) analysis carried out with a Philips CM-12 instrument. After each test samples were separated by sieving from inert component (SiC) and characterized by TEM and elemental analysis using a Carlo Erba CHNS.

2.2. Catalyst testing

The catalytic tests were conducted at atmospheric pressure in a conventional fixed bed micro reactor made in quartz. The catalyst samples (i.e. 16.0 mg) in powder form was pressed and crushed to 40–80 mesh particles diluted with a large amount of inert material (10 times in volume SiC) to minimize the thermal spot effect. It was than placed between two quartz wool plugs in the centre of a quartz tube of 4 mm internal diameter, inserted into a furnace and heated to the required temperature. Before each test, catalyst was reduced in situ at 575 K for 1 h under hydrogen flow ($F_{H_2} = 100\ cm^3$/min). Hydrogen flow rate was carefully controlled using a mass flow regulator system ASM 2500. The ethanol/water reaction mixture was vaporised and mixed with the incoming gases N_2 for SR or N_2 and O_2 for ATR conditions in a thermo-regulated vaporiser packed with SiC. The liquid feed (EtOH/H_2O) rates were controlled with high precision by an isocratic pump (HP 1100 Series). The vaporising temperature ($T = 473\ K$) was carefully selected to reach the fast vaporisation of liquid mixture, minimizing thermal reactions (i.e. ethanol dehydration). Composition of the inlet and outlet gases were analysed on-line using Hewlett-Packard 6890 Plus Gas Chromatograph equipped with a thermal conductivity detector (TCD) and three columns (Molecular Sieves 5A, Poropack Q, and Hysep). The helium ($F_{He} = 70\ cm^3$/min) was used as carrier gas, while nitrogen (10 vol.% in the inlet mixture) represented the inert standard. To test the influence of contact time on catalyst activities in SR conditions, the reaction mixture (i.e. for S/C = 4.2 mol/mol; 9.6 vol.% ETOH, 80.4 vol.% H_2O and 10 vol.% N_2), was fed in the reactor at $T = 923\ K$ varying the contact time between 0.655 s < τ_{EtOH} < 0.012 s. The effect of oxygen addition for a given S/C at $T = 923\ K$ has been also investigated, by varying the O_2/EtOH molar ratio between 0.2 and 1.1 mol/mol.

3. Results and discussion

The SR endothermicity is quite evident from Table 1 that reports some SR test in terms of ethanol conversion, enthalpy change, hydrogen yield and outlet gas composition. On the other hand, because of the deep decrease in the ethanol conversion, the heat balance varies as a function of the contact time (τ_{EtOH}) and two different regions can be defined. The first region is characterised by values of τ_{EtOH} higher than 0.048 s where the ethanol is fully converted and the process enthalpy is almost constant (about 55 kJ/mol). When the τ_{EtOH} is lower than 0.048 s, a marked decay of ethanol conversion is evident. As reported in earlier papers [9], in these conditions, only ethanol dehydrogenation is completed and other processes are not fully equilibrated. It is, also, interesting to note the absence of acetaldehyde in the outlet composition indicating that this intermediate is totally converted on Rh/Al_2O_3 by a fast decarbonylation step. At

Table 1
Ethanol steam reforming on Rh/Al$_2$O$_3$ catalysts[a]

Selectivity to carbonaceous products (%)

Contact time τ_{EtOH} (s)	Ethanol converted (%)	Enthalpy (ΔH) (kcal/mol)	CO$_2$	CO	CH$_4$	Yield to H$_2$ (Y_{H_2}) H$_{2(out)}$/EtOH$_{(in)}$	MAR$_{MSR}$ (bar^2)	MAR$_{WGSR}$ dimensionless
0.655	100.00	54.78	77.55	22.17	0.28	5.47	3.6856	2.3807
0.120	100.00	55.42	69.26	27.41	3.33	5.17	0.7933	1.8482
0.072	100.00	52.69	61.85	31.59	6.57	4.83	0.5420	2.6070
0.048	100.00	56.24	55.60	32.00	12.40	4.34	0.0825	1.0005
0.036	90.32	54.46	52.62	32.47	12.52	3.89	0.0616	0.7001
0.033	80.59	62.39	49.35	33.69	14.00	3.43	0.0720	0.8316
0.027	75.22	66.72	45.94	34.53	17.91	2.99	0.0428	0.4007
0.025	71.15	75.52	47.20	34.75	18.05	2.78	0.0172	0.3416
0.020	55.59	97.79	47.04	35.37	17.59	2.30	0.0103	0.2974
0.012	38.69	150.96	50.49	33.80	15.71	1.67	0.0057	0.2622

[a] General conditions: steam carbon molar ratio S/C = 4.2 mol/mol; T = 923 K.

last, reduction in contact time produces a significant variation in the outlet gas composition, when ethanol conversion decreases from 100 to 38.69% (τ_{EtOH} = 0.012 s). Only an experimental value of 1.67 in the hydrogen yield is reached, while 6 mol of H$_2$ can be produced for each mole of ethanol as provided by stoichiometry. The change in outlet composition leads also a great variation on the process thermicity (enthalpy variation moves from ∼55 to 150.96 kcal/mol). In summary, we observed that ethanol SR can be a promising process, but it is limited by the needs of an high heat supply. Further, as reported in previous papers [15] the coke formation can be present and fast catalyst decay has been observed. Some preliminary ATR results are reported in Figs. 1 and 2, where ethanol conversion and enthalpy changes are shown as a function of O$_2$/EtOH ratio. Firstly, it seems to be evident that the effect of oxygen is very important

both for ethanol conversion and enthalpy changes. In fact, when ethanol conversion is close to 75% at O$_2$/EtOH = 0 (no oxygen supplied) the enthalpy change is positive, while by increasing the oxygen amount in the inlet, the conversion also increases and the reaction becomes progressively exothermic. For low values of O$_2$/EtOH ratio there is not the full conversion and ethanol has been detected in the outlet gases together other secondary products like methane and acetaldehyde (Fig. 3). This is a factor indicating the ethanol dehydrogenation and acetaldehyde decomposition reactions will not reach the equilibrium, while the positive enthalpy change seems to demonstrate the steam reforming will be the dominant process at this operative conditions. Significant variation in the process mechanism arises when oxygen rate will increase. In fact, the ethanol conversion increases until to reach 100%, at O$_2$/EtOH ratio close to 0.45, and it
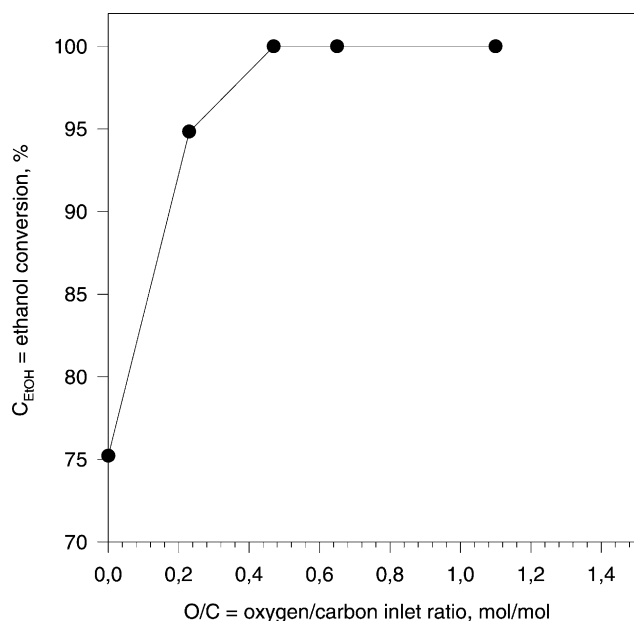

Fig. 1. Ethanol conversion vs. O/C atomic ratio on Rh/Al$_2$O$_3$ catalyst. General conditions: S/C = 8.4 mol/mol; GHSV = 150.000 h^{-1}; T = 923 K.
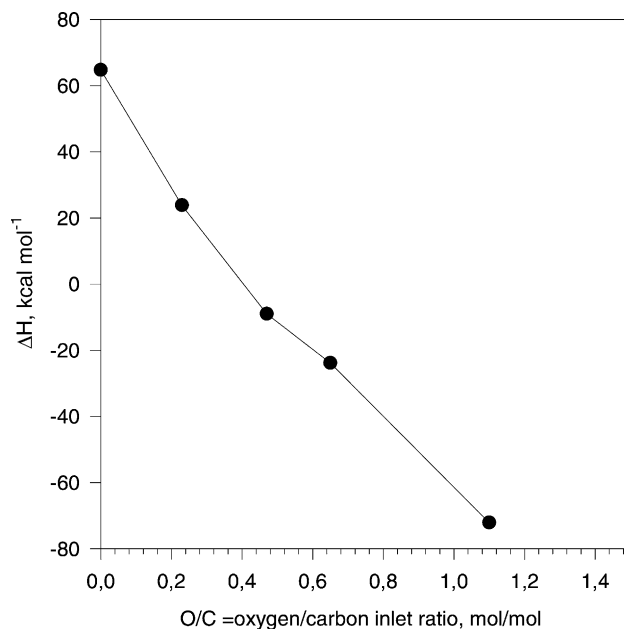

Fig. 2. Enthalpy variation vs. O/C atomic ratio, on Rh/Al$_2$O$_3$ catalyst. General conditions are reported in Fig. 1.
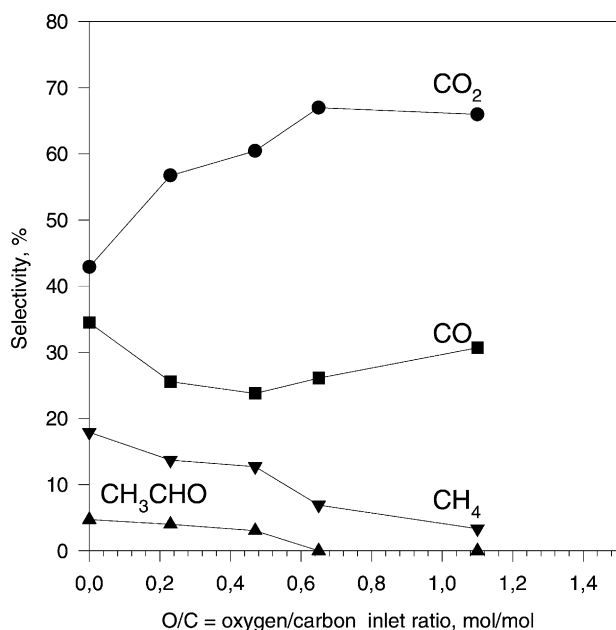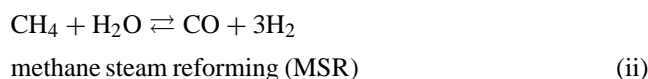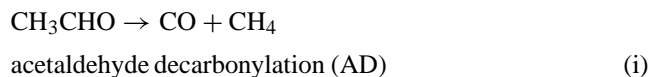
Fig. 3. Selectivities towards CO_2, CO, CH_4, CH_3CHO vs. O/C atomic ratio, on Rh/Al_2O_3 catalyst. General conditions are reported in Fig. 1.
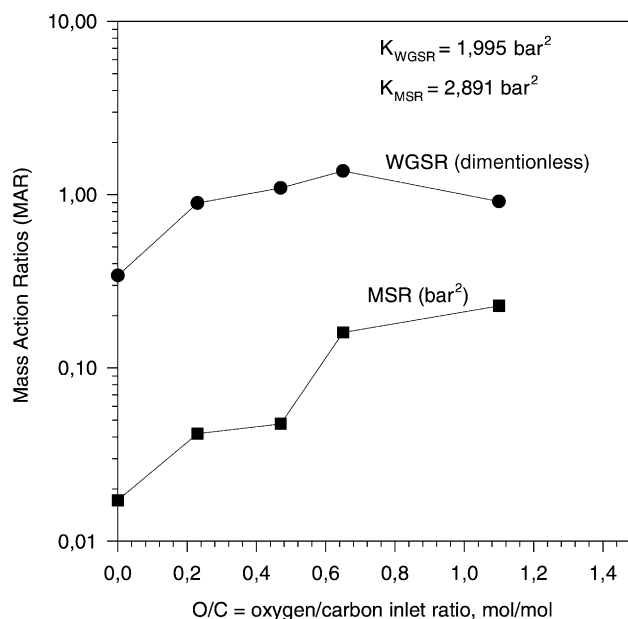

Fig. 4. Mass action ratios for methane steam reforming and water gas shift reactions (MAR_{MSR} and MAR_{WGSR}) vs. O/C atomic ratio, on Rh/Al_2O_3 catalyst. General conditions are reported in Fig. 1.

remains constant, while the enthalpy change drops to negative values (at $O_2/EtOH = 0.4$, the enthalpy change is zero and the process is adiabatic).

We believe that when oxygen percentage increases, the oxygen action becomes prevalent and it fully oxides part of ethanol, methane and acetaldehyde, simultaneously releasing heat. The steam reforming of the remaining unreacted molecules (endothermic) can be so sustained by an adequate energy amount. As reported in Fig. 3, in fact, selectivity towards CO_2, CO, CH_4, CH_3CHO is a function of the $O_2/EtOH$ ratio. It is noticeable that an increase of oxygen content in the reactants composition produces an enhancement of CO_2 and in the meantime, a lowering of those of CH_4 and CH_3CHO. The CO remains almost constant, close to the initial value of 35 vol.%, with only a little lowering at intermediate $O_2/EtOH$ ratios.

All these observations can be rationalised by the mechanism proposed in an earlier paper [9] on ethanol SR. The CO formation can be mainly attributed to the following reactions:

$$CH_3CHO \rightarrow CO + CH_4$$

acetaldehyde decarbonylation (AD)   (i)

$$CH_4 + H_2O \rightleftarrows CO + 3H_2$$

methane steam reforming (MSR)   (ii)

While its disappearance is attributable to the "water gas shift reaction (WGSR)".

$$CO + H_2O \rightleftarrows CO_2 + H_2 \qquad \text{water gas shift reaction} \quad \text{(iii)}$$

Obviously also reverse reactions must be taken into account, because reactions (ii) and (iii) represent chemical equilibria (see below).

In ATR process, the oxygen content seems to influence the CO formation. In fact, for low contents of O_2, the WGSR is faster than reactions (i) and (ii) and the CO oxidation (CMO) (iv) prevails on its formation:

$$CO + \tfrac{1}{2}O_2 \rightarrow CO_2 \qquad \text{carbon monoxide oxidation} \quad \text{(iv)}$$

Higher amount of O_2 in the inlet gases produces, in the first step, an equivalent big amount of CO_2, that by mass action moves to left the equilibrium reaction.

By plotting the mass action ratios for reactions (ii) and (iii) (MAR_{MSR} and MAR_{WGSR}) as a function of $O_2/EtOH$ ratio (Fig. 4) we can better understanding the mutual influence of reaction rates.

From these curves, it is immediately noticeable that WGSR is very close to its equilibrium ($K_{WGSR} = 1.995\ bar^2$) and its trend is almost constant. On the contrary, MAR_{MSR} appears to be much lower than the equilibrium value ($K_{MSR} = 2.891\ bar^2$) even if the trend increases directly with the O_2 content in the feed.

The conventional defined "hydrogen yield" (Y_{H_2}) as a function of $O_2/EtOH$ ratio and for different S/C ratio values is shown in Fig. 5. As evident from the volcano shaped plots, a proper amount of oxygen in the inlet stream improves the H_2 production until a maximum is reached. In fact, if a small amount of oxygen is inadequate to fully convert the feed and to compensate the endothermicity of the SR reaction, a strong excess of oxygen burns everything to CO_2 and H_2O. Obviously, by increasing the water inlet both equilibria (ii) and (iii) move to the right and hydrogen yields are
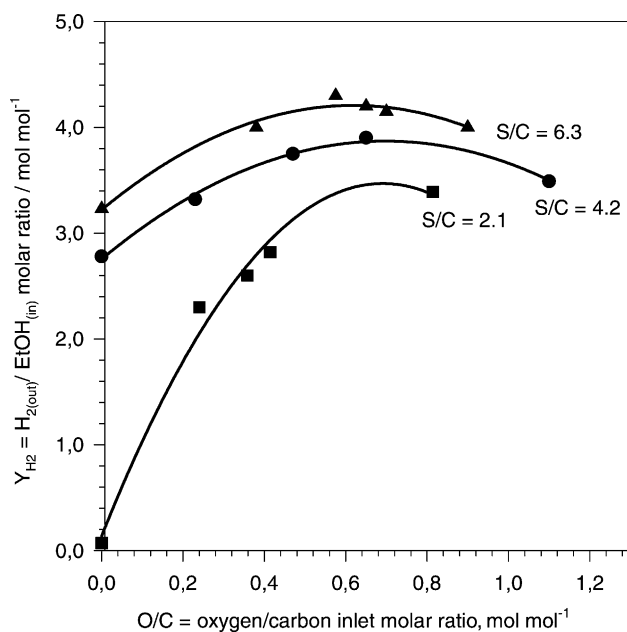
Fig. 5. Moles of produced H_2 per mol of "feed" ethanol (Y_{H_2}) vs. O/C and S/C molar ratios, on Rh/Al_2O_3 catalyst. General conditions are reported in Fig. 1.

Fig. 6. Moles of produced H_2 per mol of "converted" ethanol vs. O/C and S/C molar ratios, on Rh/Al_2O_3 catalyst. General conditions are reported in Fig. 1.

consequently increased. On the other hand, for practical purposes, a strong excess of water can be not fully convenient because of the too high heat recycle required and we found that an S/C ratio close to 4.2 can represent a good compromise.

The Y_{H_2} reported in Fig. 5 well represents the ATR performance in the spite of practical purposes, but it does not give clear information to evaluate the reaction mechanism. In fact, because of the calculation method, it takes simultaneously into account both ethanol conversion and selectivity to the various products, without distinguish among the various effects. More interesting, from the speculative point of view, is to report the "hydrogen selectivity" (S_{H_2}) when H_2 outlet is referred to the "converted" ethanol instead to the total ethanol "feed". The S_{H_2} versus the O_2/EtOH ratio is reported in Fig. 6. As shown, without taking into account the conversion, no marked influence exists on the S_{H2} attributable to the O_2 feed, and only the S/C ratio little influences the reaction pathway. Obviously, the S_{H_2} increases by increasing the S/C ratio, but also without a strong water excess (S/C = 2.1 mol/mol) or oxygen addition (SR condition), hydrogen selectivity is still close to S_{H_2} = 3 mol/mol. Thus, notwithstanding some coke is formed when S/C = 2.1 mol/mol, the same reaction mechanism than at ATR conditions seems to occur.

As reported in previous papers [14–17], the catalysts used in SR–ATR conditions lost their activity because of three different causes: (a) coke deposition; (b) active phase sintering; (c) metal oxidation.

The post-mortem analyses carried out on samples of different family of catalysts bring us to suppose Co based catalysts strongly suffer oxidation of active phase [14], instead,
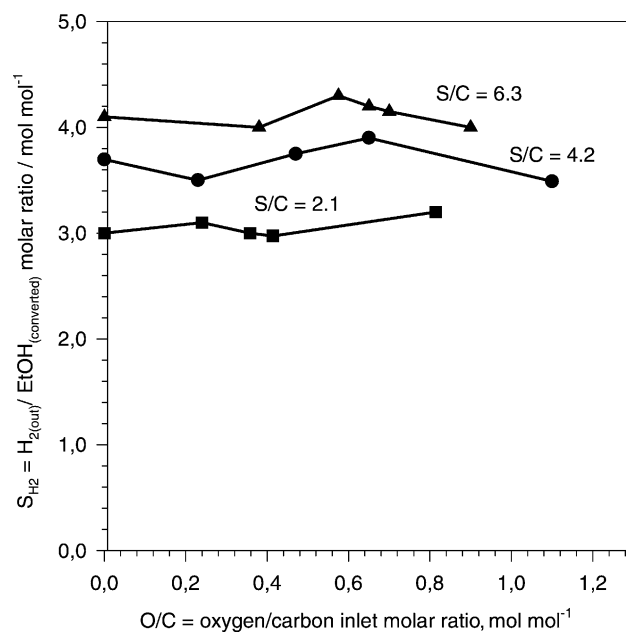
Ni promotes a massive deposition of coke that fast deactivates the catalyst, and Rh shows a strong sintering.

As evident from TEM micrographs, reported in Fig. 7, the Rh catalyst, used in ATR, shows a growing of metal particles until 80–90 A°.

This data is in agreement with those reported in a previous paper [15], where it has been observed, after 100 h on stream in ATR condition, the formation of larger and broader particles.

This effect has not been detected under SR conditions (absence of oxygen), where Rh crystallites (10–55 Å) have been detected in size almost close to those of the fresh catalyst.

In ATR condition, the selectivity is also affected by the sintering. In fact, after 100 h on stream a change in product selectivities brings the system toward a lowering in the hydrogen yield (Y_{H_2}).

On the other hand, as reported in a previous paper [15], the use of some oxygen in the feed produces an appreciable improvement in the catalyst life-time if compared to the results obtained in SR ambient in which the ethanol conversion drops until the 50% of its initial value. Further, a very clean catalytic surface has been found also after 100 h on stream, when ATR conditions are adopted (Fig. 7).

Some considerations emerge about the carbon formation mechanisms evidenced on the Rh tested catalysts. The TEM analyses has demonstrated that "shell encapsulating" carbon is formed under SR condition. At contrary, on ATR stream, a small amount of carbon whiskers has been found, but in any case, no shell encapsulating or pyrolytic carbon has been detected [18]. Between the two types of carbon, certainly, the "shell encapsulating" ones greatly affects the catalytic activity, because of its inclusion of active sites. The whiskers
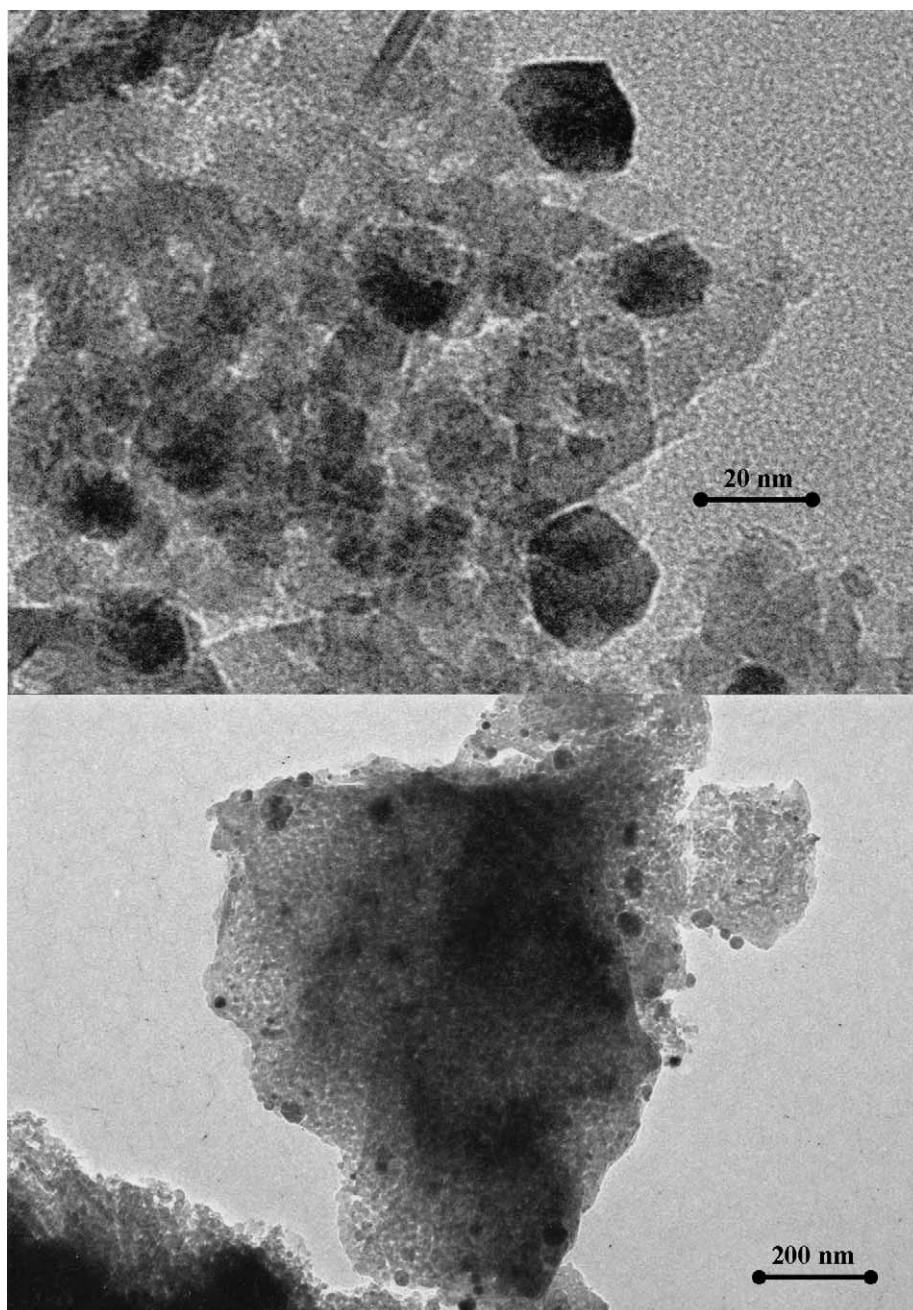
Fig. 7. TEM micro-photographies on the Rh/Al$_2$O$_3$ catalyst after $\tau = 100$ h in ATR conditions. O/C = 0.41 mol/mol and general conditions are reported in Fig. 1.

formation, instead, has a minor effect and the particles still maintain cleanliness of their active surface.

The small presence of coke on the exhausted catalyst, seems to highlight a mechanism of auto-cleaning of the catalytic surface by the oxygen, which provides to regenerate the metal surface.

From this considerations, the only undesirable effect attributable to the presence of the oxidative environment is the metal particle growing [15], probably. The persisting of oxidative conditions are clearly evidentiated by the remarkable increase in the production of CO$_2$ (total oxidation product).

On the basis of these considerations, the sintering of the Rh is attributed to an ATR mechanism which foresees the "hot spots" action on the surface of the metal. Such a mechanism is correlated with the partial or total combustion of the coke and with the action of adsorbed molecules on the surface of the Rh crystallites (ethanol, acetaldehyde, methane, CO and H$_2$) that promotes the migration of Rh particles into bigger crystals. In these conditions, even though the dehydrogenation function is compromised, the catalytic "oxidative" function seems to retained for a longer time with increase of CO$_2$ production.

4. Conclusions

This paper quite demonstrates that auto-thermal reforming can be an attractive catalytic process able to produce H_2 from bio-ethanol. The 5% Rh/Al_2O_3 catalyst, homemade, shows a good performance, also without oxygen addition, but a little amount of O_2 in the inlet mixture greatly increases the overall hydrogen yield (Y_{H_2}). Without oxygen (SR condition) higher temperatures and contact times are needed, and the risk of coke formation is always present. On the other hand, by increasing the O_2/EtOH inlet molar ratio, also the CH_4 formation is strongly reduced and only few H_2 can be produced. Further, when the oxygen amount is too high, the ethanol total oxidation produces a strong local temperature increase (hot spots) and Rh crystallites sinter.

At last, we have no evidence of a change on mechanism in presence of oxygen. In fact, although the selectivity to each carbonaceous product can varies, the overall selectivity to H_2 (S_{H_2}) is almost retained, independently to the gaseous environment (oxidative/reductive).

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