High efficiency steam reforming of ethanol by cobalt-based catalysts

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Abstract

The steam reforming of ethanol was studied at $400\,^\circ$C on Co/Al_2O_3 and Co/SiO_2 catalysts with a cobalt content of 8 and 18% (w/w), respectively. Catalysts were prepared by the impregnation method and characterized by atomic absorption spectroscopy, Raman spectroscopy, and temperature-programmed reduction with hydrogen. The results indicated the presence of Co_3O_4 as the main phase of cobalt and CoO_x species interactions with alumina. The catalysts showed average conversion higher than 70% for the steam reforming of ethanol at $400\,^\circ$C. The increase of ethanol conversion and reduction of the amount of liquid products were observed for the catalysts with higher cobalt contents. The CO concentration in the gaseous mixture is reduced to 800 ppm levels for the Co/Al_2O_3 catalyst with 18% of cobalt. During ethanol reformation, the CO produced can react with water (water gas shift, WGS) or hydrogen (methanation, without water) on Co sites. Both reactions, WGS and methanation, allows high conversion on the Co/Al_2O_3 and Co/SiO_2 catalysts, but Co/Al_2O_3 shows better CO removal.
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1. Introduction

Fuel cells have been investigated as devices for the direct conversion of the chemical energy of a fuel into electrical energy, with high efficiency. Polymer electrolyte fuel cells (PEFCs) are considered for applications as power supplies for vehicles and small generators, owing to several advantages including compact size, easy start-up and shut-down, and high power density. In many practical cases, the hydrogen needed for the PEFC operation is obtained as a hydrogen-rich gas produced by on-board reforming of another fuel [1]. In Brazil, because of high ethanol production there is a strong interest in the development of ethanol steam reforming systems in order to couple a fuel cell device.

The use of biomass-derived ethanol for hydrogen production is very attractive because of its relatively high hydrogen content, non-toxicity, and safe storage and handling. It is a renewable fuel, which does not contribute to an increase in the Earth's greenhouse effect [2–4]. The problem with the ethanol reforming process is that, beside formation of H_2, CO_2, H_2O and CH_4, the gaseous fuel produced usually contains high levels of CO, which is a strong poison for the hydrogen oxidation reaction taking place on the anode of the PEFC. Even with more advanced anode catalysts, the system cannot accept more than 100 ppm for efficient operation [5].

The production of highly purified hydrogen with respect to the CO content increases the system weight and volume and the fuel cost, because of the requirement for complex multi-stage processes (water gas shift reaction (WGSR) and preferential oxidation of CO (PROX)), or a membrane CO filter [6,7]. The water gas shift reaction,

$$CO + H_2O \rightleftharpoons H_2 + CO_2 \tag{1}$$

is an exothermic process, implying that the equilibrium conversion of carbon monoxide is favored at lower temperatures. Two catalysts are used industrially to promote the WGSR: a high-temperature shift catalyst, FeCr (350–$500\,^\circ$C) and a low-temperature shift catalyst, CuZn (150–$250\,^\circ$C), with the WGS reactor placed in series with the reforming device [4]. An additional clean-up step is required for PEFC applications and this is the PROX in which the CO content is lowered to less than 20 ppm by the preferential oxidation of CO with oxygen:

$$2CO + O_2 \rightarrow 2CO_2 \tag{2}$$

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This process is conducted using a selective supported noble metal catalyst, but there is the disadvantage of hydrogen consumption [8]:

$$2H_2 + O_2 \rightarrow 2H_2O \qquad (3)$$

Because of these problems, it is of great interest that the gas leaving the reforming reactor has a minimum content of CO. Recently, Liguras et al. [2] studied supported Rh, Ru, Pt, and Pd catalysts for ethanol steam reforming at temperatures, from 600 to 800 °C. It was found that Rh is significantly more active and selective toward H_2 and CO formation. Cavallaro et al. [9] observed total conversion of ethanol on Rh/Al_2O_3 at 650 °C, with production of 40 and 10% of CO and CH_4, respectively. In agreement with thermodynamic equilibrium predictions, the increase of temperature resulted in an increased of the CO amount in the reformed gas [10].

Ethanol steam reforming at 400 °C on supported transition metal catalysts (Ti, Zr, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sb, Ru, Pt, or Rh) was investigated by Haga et al. [11]. It was concluded that Co/Al_2O_3 was the more selective catalyst for the overall reforming reaction

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \qquad (4)$$
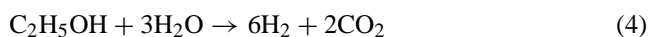
Showing 8 and 6% of CO and CH_4, respectively. Recently, it was found that supports with acid properties such as Al_2O_3 and with low Co loadings promote the dehydration of ethanol to produce significant amounts of ethylene [12]. On the other hand, cobalt-SiO_2 or cobalt-MgO catalysts prevent the formation of ethylene, but the product distribution (H_2, CO, CO_2 and CH_4) depends on the reaction conditions [13]. In these studies the amount of CO produced in the reforming process ranged from 2 to 20%, which are far above the levels tolerated by a PEFC system.

This paper presents results of a study of the product distribution in the steam reforming of ethanol on supported cobalt catalysts. The effects of parameters such as the spatial velocity, the nature of the catalyst support, and the Co loading were investigated with the aim of minimizing the CO amount in the reformate gas. The potential of Co-supported catalysts for promoting the WGS and methanation reactions is discussed.

2. Experimental

The Co/γ-Al_2O_3 and Co/SiO_2 catalysts were prepared by the incipient wetness impregnation of the γ-Al_2O_3 (Degussa) and SiO_2 (Aerosil 200, Degussa) support, using an aqueous solution of $Co(NO_3)_2 6H_2O$ (98%, Aldrich). The excess water was removed in a rotating evaporator and the samples were dried at 110 °C. The catalysts were then obtained by calcination of the samples in air at 600 °C for 6 h.

The catalysts were characterized by atomic absorption spectroscopy (AAS), Raman spectroscopy and temperature-programmed reduction with hydrogen (H_2-TPR).

The measurements of Raman spectroscopy were accomplished in a Renishaw spectrometer. The spectra were collected between 150 and 850 cm^{-1}, using a beam of a red helium–neon laser (632.8 nm and diameter of 1 mm) of 0.070 mW, with the sample exposed to the air under ambient conditions. The H_2-TPR analyses were performed to determine the reduction behavior of the cobalt species on the different supports. These experiments were carried out in a Micromeritics 2705 equipment, using 50 mg of catalyst and a temperature ramp from 25 to 1000 °C at 10 °C/min. A flow rate of 30 cm^3/min of 5% H_2 in N_2 was used for the reduction. A thermal conductivity detector (TCD) was employed to determine the amount of hydrogen consumed. A cold trap (-50 °C) was placed before the detector to remove the water produced during the reduction.

Catalytic performance tests have been carried out using an apparatus consisting of a flow controller system, the reactor unit and the analysis system. The flow system is equipped with a set of mass-flow controllers (Allborg 4 channel), which accurately control the flow of the gases (He, N_2, H_2, etc.) entering the reactor. The catalyst was placed in a fixed-bed system inside a continuous flow micro-reactor (13 mm diameter). The operating temperature was controlled by a thermocouple placed inside the oven and close to the reactor wall, to assure precise temperature measurements during the pretreatment and reaction steps. Prior to the reforming experiments, the catalyst (typically 150 mg) was activated by in situ reduction in flowing H_2 (40 cm^3/min) at 650 °C (10 °C/min) for 1 h. After this step, the sample was cooled down to 400 °C under a pure N_2 flow. Then, the reaction was started in a H_2-free environment feeding a 52% ethanol solution ($1EtOH:3H_2O$ molar ratio) at a flow rate of 3 cm^3/h. The liquid solution was pumped to a vaporizer where the reagents were heated to 150 °C and then fed to the reactor at a pressure of 1 atm.

The analyses of the gaseous products were carried out *on-line* by gas chromatography (Varian, Model 3800) with two thermal conductivity detectors. The reaction outlet stream was divided into two aliquots inside an automated injection valve, and then analyzed in a different way in order to obtain accurate and complete quantification of the reaction products. One of the aliquots was used to analyze hydrogen and methane, which were separated using a $13\times$ molecular sieve (3 m $\times$ 1/8 in.) packed column, using nitrogen as carrier gas. The other aliquot was used to analyze CO_2, CH_4, CO and C_2H_4. Helium was used as carrier gas and separation was accomplished by using a porapak N (2 m $\times$ 1/8 in.) and a $13\times$ molecular sieve (3 m $\times$ 1/8 in.) packed columns. The lower limit for carbon monoxide detection was 200 ppm. The residual reagents and the liquid products ($C_2H_5OC_2H_5$, CH_3CHO, CH_3OCH_3, $CH_3CO_2C_2H_5$ and CH_3COOH) were condensed in the reactor outlet. At the end of the catalytic test, the flow of ethanol and water was stopped and the liquid condensate was analyzed by gas chromatography. Helium was used as a carrier gas and the separation and quantification were attained by a HP-FFAP capillary column (25 m,

dimeter = 0.2 mm) and a flame ionization detector. The av-
erage ethanol conversion was calculated using the ethanol
concentration as ([EtOH]$_{in}$ − [EtOH]$_{out}$)/[EtOH]$_{in}$.

3. Results and discussion

Table 1 shows the chemical composition obtained by
AAS of the supported cobalt catalysts after calcination at
650 °C. Results indicate a very good agreement of these val-
ues with the initial formulation of the precursor solutions.
Following these data, the catalysts will be designated as
Co(8)/Al$_2$O$_3$, Co(18)/Al$_2$O$_3$, Co(8)/SiO$_2$, and Co(18)/SiO$_2$,
where the numbers represent the approximate mass per-
centage of cobalt. Fig. 1 shows the Raman spectra obtained
for these catalysts and for Co$_3$O$_4$. In all spectra the only
bands are at 197, 484, 524, 620 and 690 cm^{-1}, which refers
to Co$_3$O$_4$ vibrations. The presence of Co$_3$O$_4$ in the surface
of the samples, prior to the H$_2$-treatment in the reforming
reactor, agrees with results reported previously [12,14].

Temperature-programmed reduction with H$_2$ (H$_2$-TPR) is
a powerful tool to study the reduction behavior of oxidizes
phases, as e.g. Co$_3$O$_4$. In some cases it is also possible
from the reduction profiles of supported oxides to obtain
useful information about the degree of interaction of the
oxide phase with the support. Results of the H$_2$-TPR anal-
yses of the calcinated Co/Al$_2$O$_3$ and Co/SiO$_2$ catalysts are
presented in Fig. 2. The H$_2$-TPR profile for the Co(8)/SiO$_2$
catalyst shows a shoulder at 370 °C and a principal peak
at 400 °C, which are attributed to the reduction of Co$_3$O$_4$

Table 1
Chemical characteristics of the calcinated supported cobalt catalysts

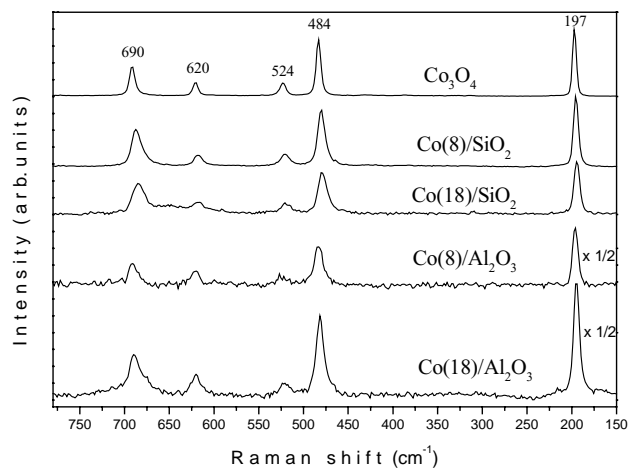| Catalysts	Co content (wt.%)
Co(8)/Al$_2$O$_3$	8.6
Co(18)/Al$_2$O$_3$	18.7
Co(8)/SiO$_2$	7.8
Co(18)/SiO$_2$	18.2

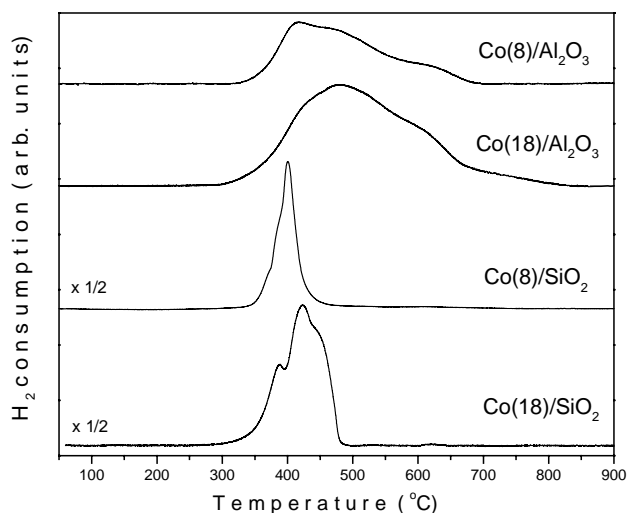Fig. 1. Raman spectra for the supported cobalt catalysts and for Co$_3$O$_4$.

Fig. 2. H$_2$-TPR profiles for the Co/Al$_2$O$_3$ and Co/SiO$_2$ catalysts.

to CoO and subsequent reduction of CoO to metallic Co,
respectively. For Co(18)/SiO$_2$ these peaks are shifted to 390
and 425 °C, suggesting an increase of the mean size of the
Co$_3$O$_4$ particles. Slower hydrogen diffusion into the bulk of
the larger particles is probably the cause of the peak shifts
and the appearance of the shoulder at 450 °C.

In the case of the Co/Al$_2$O$_3$ catalysts, one main reduction
peak at about 400 °C and two broad reduction features at
480 and 600 °C are observed, suggesting the presence of Co
species with different degrees of interaction with the sup-
port. The Co(8)/Al$_2$O$_3$ catalyst shows a reduction peak at
400 °C attributed to Co$_3$O$_4$ reduction directly to metallic Co.
This peak is shifted to 430 °C for Co(18)/Al$_2$O$_3$ due to the
higher Co content or larger particle sizes, as already men-
tioned for Co/SiO$_2$. The reduction peaks at 480 and 600 °C
observed only for the Co/Al$_2$O$_3$ catalysts must correspond
to the reduction of CoO$_x$ going to metallic Co, for sites
presenting strong cobalt-support interactions. Arnoldy and
Moulijn [15] had attributed the peaks at 480 and 600 °C to
the presence of Co$_3$AlO$_6$ (Co$_3$O$_4$-AlO$_2$) and Co^{2+}-Al$_2$O$_3$
species, respectively. These peaks are absent for the Co/SiO$_2$
catalysts, showing that in this case there is no interaction of
the Co-species with the support.

The area below all reduction peaks in the TPR increases
with the increase of the Co load, and the proportion is
in accordance with the catalyst compositions, as measured
by AAS (Table 1) for the two systems. Integration of the
H$_2$-TPR peaks leads to values of H$_2$/Co molar proportions
of 1.30 and 1.37 for the Co/AlO$_3$ and Co/SiO$_2$ catalysts,
respectively. These values are consistent with the theoreti-
cal H$_2$/Co molar ratio for Co$_3$O$_4$ (1.33), confirming, within
the experimental errors, that this is the main species of the
cobalt phase.

Table 2 shows the values of the total molar conversion
percentage of ethanol, the conversion percentages of ethanol
only to gases, and the composition of the liquid conden-

Table 2
Percentage of ethanol conversion on supported cobalt catalysts obtained at 400 °C

Catalysts	Ethanol conversion (molar %)	Liquid conversion to gases[a] (%)	Composition of liquid condensate (%)	
			Water	Other products
$Co(8)/Al_2O_3$	74	67	71.3	28.7
$Co(18)/Al_2O_3$	99	87	99.6	0.4
$Co(8)/SiO_2$	89	71	67.4	32.6
$Co(18)/SiO_2$	97	87	98.0	2.0

[a] $X = 100(V_{in} - V_{out})/V_{in}$, where $V = V(H_2O) + V(EtOH)$.

sates for all reduced catalysts, for experiments conducted with the reformer reactor at 400 °C. It is observed that all supported cobalt materials show an average conversion of ethanol higher than 70%. It is also noted that the conversion percentage increases with the increase of the cobalt content, reaching virtually 100% for catalysts with 18% of cobalt on both supports. In agreement with this, formation of liquid products ($C_2H_5OC_2H_5$, CH_3CHO, CH_3OCH_3, $CH_3CO_2C_2H_5$, and CH_3COOH) is negligible for these systems, as shown in Table 2. The increase of ethanol conver-

sion and the reduction of the amount of liquid products are observed for the catalysts with higher cobalt contents.

Figs. 3 and 4 show the distribution of the gaseous products as a function of time, for the steam reforming of ethanol at 400 °C on the reduced Co-based catalysts. In all cases formation of only H_2, CH_4, CO, and CO_2 is detected, with the production of hydrogen ranging from 60 to 70%, except for the $Co(8)/Al_2O_3$ catalyst for which, in agreement with previous results [12], formation of some ethylene is noted.

Formation of the main reforming products of ethanol may be made by the following reactions:

$$C_2H_5OH + 3H_2O \rightarrow 6H_2 + 2CO_2 \qquad (4)$$

$$C_2H_5OH + H_2O \rightarrow 4H_2 + 2CO \qquad (5)$$

$$C_2H_5OH \rightarrow CH_4 + CO + H_2 \qquad (6)$$

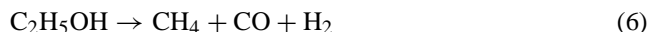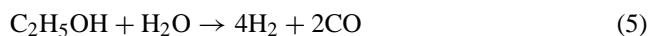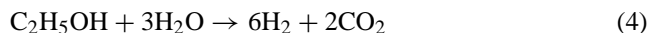$$CO + 3H_2 \rightleftharpoons CH_4 + H_2O \qquad (7)$$

Fig. 3 shows that for both supported catalysts there is smaller production of methane for the catalysts with higher cobalt content. It is also noted that, for the catalysts with 8% of Co, the amounts of methane and CO are essentially the
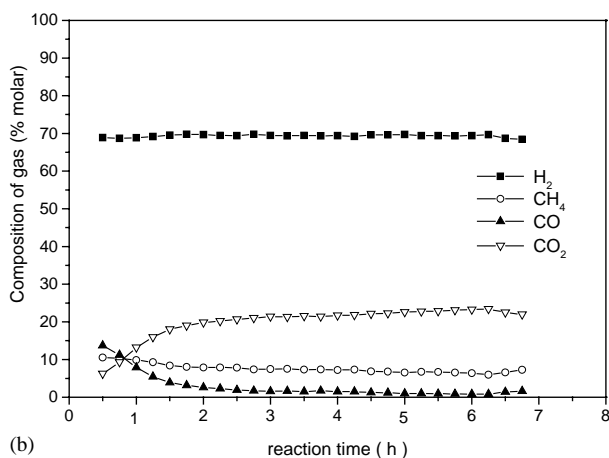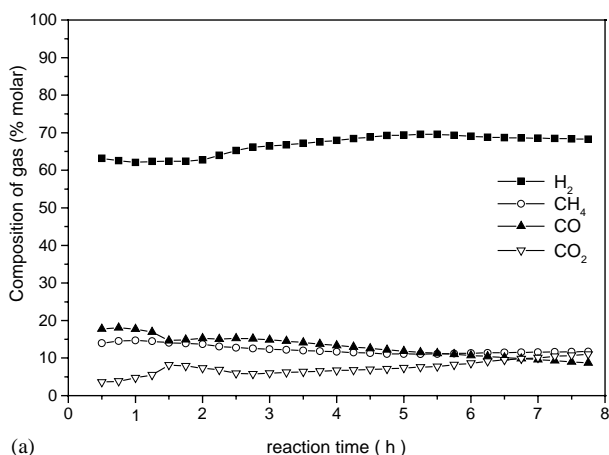

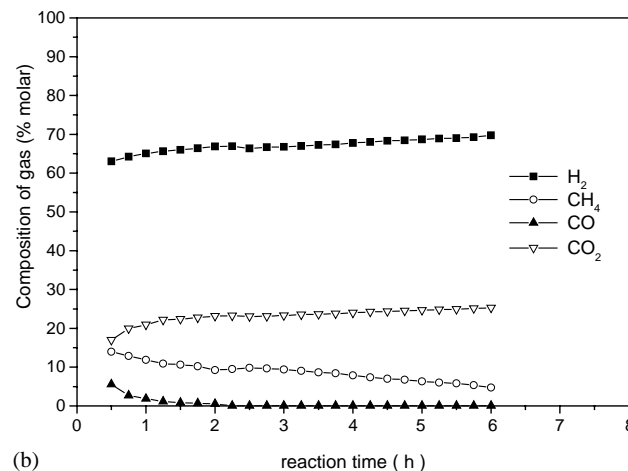Fig. 3. Product distribution of the steam reforming of ethanol at 400 °C on: (a) $Co(8)/SiO_2$ and (b) $Co(18)/SiO_2$.
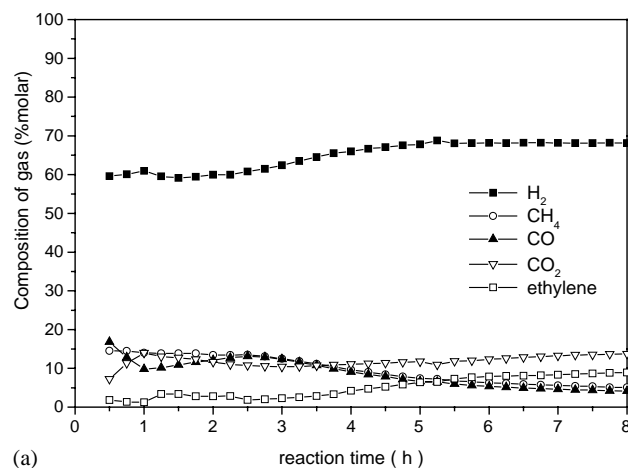

Fig. 4. Product distribution of the steam reform of ethanol at 400 °C on: (a) $Co(8)/Al_2O_3$ and (b) $Co(18)/Al_2O_3$.

same along the total duration of both experiments, suggesting that reaction (6) may be responsible for the formation of both CO and CH_4, because it provides the same stoichiometric amounts for these products. Generally, the increase of the cobalt content on both support leaded to a significant lowering of CO formation. For the catalysts with 18% of cobalt, the CO content was of the order of 5–15% in the beginning of the experiments, but this initial value decreases drastically as a function of time reaching 0.08% (800 ppm) on $Co(18)/Al_2O_3$ for $t > 2$ h. It is also observed that the decrease of the CO content as a function of time was accompanied by an increase of the CO_2 content, indicating that the cobalt sites are acting both for the ethanol reforming (reactions 4 and 5) and for the WGS process (reaction 1).

Fig. 5 shows the product distributions for the steam reforming of ethanol, for the reactor at 400 °C loaded with amounts of $Co(18)/Al_2O_3$ (100 and 250 mg) different from that for Fig. 4b (150 mg). Results for the reactor with 100 mg (Fig. 5a) show CO contents of about 5%, while for 250 mg (Fig. 5b) the CO formation is very small (800 ppm, for $t >$

3 h) and essentially the same as with 150 mg (Fig. 4b). Thus, low catalyst loadings may not provide enough sites for occurrence of the WGS reaction (1). For the experiment with 200 mg of $Co(18)/SiO_2$, the results indicate that there is an increase in the CH_4 formation as a function time, together with a decrease in H_2 formation. This implies that there is an increase of the contribution of reaction (7) for the CO removal with a consequent decrease of the contribution of reaction (1).

Experiments were also made at 400 °C for the reactor with the $Co(18)/Al_2O_3$ and $Co(18)/SiO_2$ catalysts (150 mg), fed with a H_2/CO mixture containing 1000 ppm of CO with and without water vapor. Fig. 6 presents these results. It is seen that in absence of water large amounts of methane are formed, particularly for the Al_2O_3-supported catalyst, while the CO_2 production is negligible. As soon as water vapor is supplied to the system, there is an inversion of the CH_4/CO_2 relative distribution for both catalysts. Since the production of CO during the reforming of ethanol is made in the presence of water, these results confirms that methane
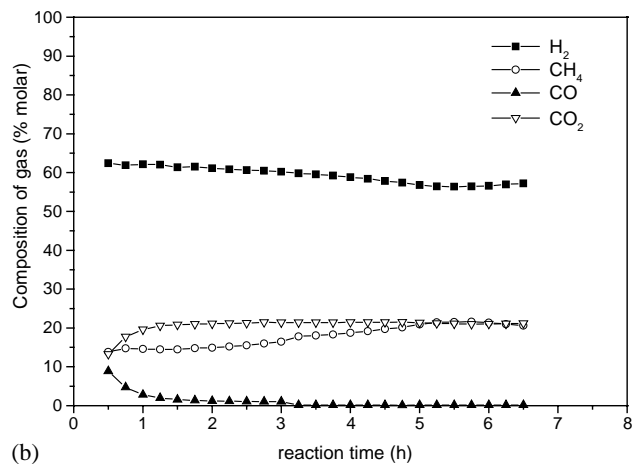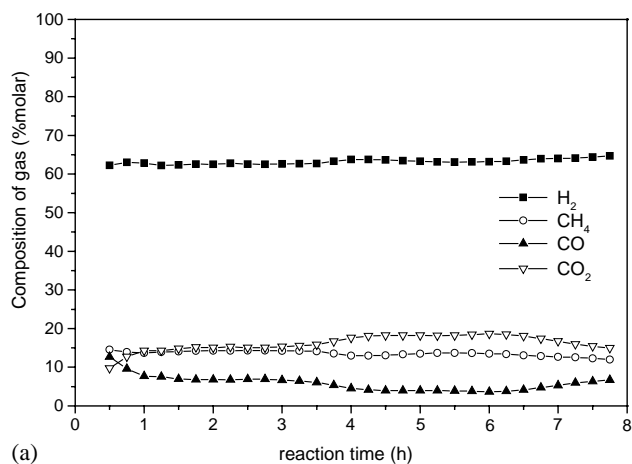

Fig. 5. Product distribution of the steam reform of ethanol on the $Co(18)/Al_2O_3$ catalyst with different masses loaded to the reactor: (a) 100 mg (conversion of 84.3%) and (b) 250 mg (conversion of 100%).
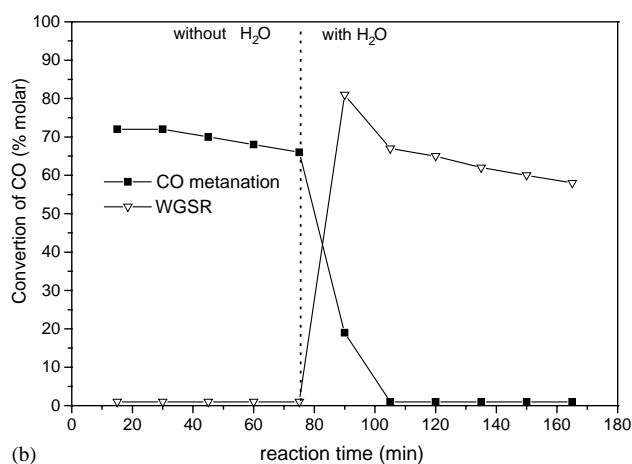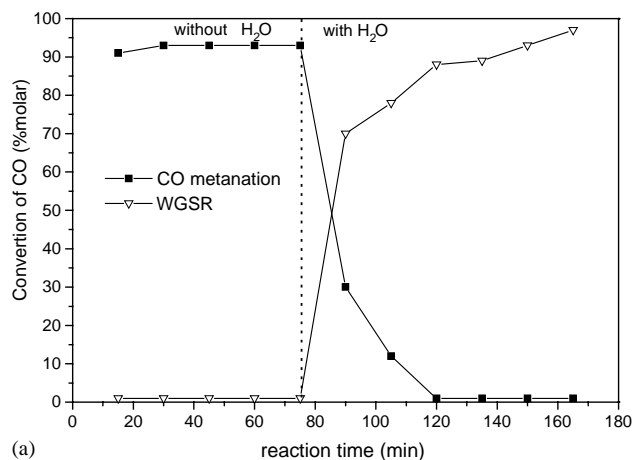
Fig. 6. Formation of CO_2 and methane during the reaction of $H_2/1000$ ppm CO at 400 °C, in the presence and absence of water vapor: (a) $Co(18)/Al_2O_3$ and (b) $Co(18)/SiO_2$ catalysts.

is mainly produced by the ethanol decomposition (reaction 6), while the CO decomposition is promoted by the WGS process (reaction 1).

Finally, it has to be noted that the levels of CO near to 800 ppm are a quite satisfactory result, for applications to PEFC. The lower CO level occurs with almost 100% of ethanol conversion, but with the production of non-negligible quantities of methane (5–10%). This product passes through the fuel cell without affecting the anode performance and, after leaving the system, it can be burned in the reforming device to provide the required heat for the endothermic reforming process.

4. Conclusions

The Co/Al_2O_3 and Co/SiO_2 catalysts after calcination at $600\,^{\circ}C$ show Co_3O_4 as the main phase containing cobalt. The reduction of this oxide to metallic Co occurs on silica or alumina at temperature near to $400\,^{\circ}C$, but a CoO_x species is observed in the case of alumina.

Co/Al_2O_3 and Co/SiO_2 catalysts had shown average conversions, higher than 70% for the steam reforming of ethanol at $400\,^{\circ}C$. An increase of ethanol conversion and reduction of liquid products were observed on the catalysts with higher cobalt contents. Hydrogen is the main constituent of the reaction effluent, which also contains CO, CO_2, and CH_4. Ethylene formation occurred only on the Co/Al_2O_3 catalyst with small Co contents ($\leq 8\%$). The CO concentration in the gaseous mixture is reduced to 800 ppm levels for the $Co(18)/Al_2O_3$ catalyst for $m \geq 150$ mg. After ethanol reforming, the CO produced can react with water (WGS) or hydrogen (methanation) on Co sites. Both reactions show high conversion on Co/Al_2O_3 and Co/SiO_2 catalysts, but Co/Al_2O_3 shows higher efficiency for CO removal.

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