

Characterization of the activity and stability of supported cobalt catalysts for the steam reforming of ethanol

Marcelo S. Batista, Rudy K.S. Santos, Elisabete M. Assaf, José M. Assaf, Edson A. Ticianelli*

Instituto de Química de São Carlos—USP, Caixa Postal 780, 13560-970 São Carlos, SP, Brazil

Received 14 April 2003; accepted 10 May 2003

Abstract

This paper reports results of studies of the catalytic activity and stability of supported cobalt catalysts for steam reforming of ethanol. Co/Al₂O₃, Co/SiO₂, and Co/MgO catalysts were prepared by an impregnation method and characterized by X-ray diffraction, atomic absorption spectroscopy, Raman spectroscopy, and temperature programmed reduction with hydrogen. The results showed the presence of Co₃O₄ and CoO_x species interacting with Al₂O₃ or MgO and formed after a calcination step. It was evident that only Co⁰ sites are active for the steam reforming of ethanol. All materials showed high levels of ethanol conversion, with molar yields of about 70% of hydrogen and 30% of CO + CO₂ + CH₄ in the gaseous mixture. The Co/Al₂O₃ catalyst also produced ethylene through a dehydration reaction of ethanol. It is proposed that the methane formation on Co/SiO₂ catalysts occurs by methanation of CO and by ethanol decomposition. After 9 h of reaction, 14–24% (w/w) of carbon was deposited on all catalysts, indicating that a well characterized deactivation of the materials is due to coke deposition.

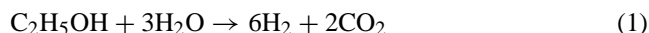
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Keywords: Ethanol; Steam reforming; Cobalt catalyst; Hydrogen production; Fuel cell

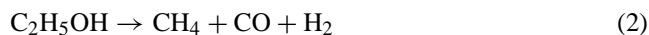
1. Introduction

Due to environmental pollution problems and the high dependence on fossil fuels, the recent world-wide interest in the energy area is strongly focused on the development of alternative fuels. Among several possibilities, the production of hydrogen from steam reforming of alcohols could favor the use of hydrogen as an alternative fuel, because it does not require gaseous hydrogen storage and distribution. The steam reforming of methanol has been thoroughly studied in recent years [1–3], but the main drawback is its relatively high toxicity. In contrast, ethanol is less toxic and could be considered a renewable fuel capable of being produced from biomass. Besides this, it does not contribute to the increase of the greenhouse effect since the steam reforming of ethanol releases the same amount of CO₂ as that absorbed by the biomass [4].

Haga et al. [5] had studied the catalytic properties of Ti, Zr, Cr, Mn, Fe, Co, Ni, Cu, Zn, Cd, Sb, Ru, Pt or Rh, supported on Al₂O₃ for ethanol steam reforming at 400 °C, and concluded that Co/Al₂O₃ catalyst showed more selectivity for the overall reaction:



These authors in another paper [6] studied Co catalysts on different supports (Al₂O₃, SiO₂, MgO, ZrO₂ and C) for the ethanol steam reforming, for 3 h. It was observed that production of methane occurred through decomposition of ethanol:



or by methanation of the CO:



Ethanol steam reforming on Cu/SiO₂, Co/MgO and Co/ZrO₂ was accompanied by methanation, while on Co/Al₂O₃ and Co/C, the methane seems to be produced by decomposition of ethanol. The thermodynamic shows that this last reaction (reaction 2) is favored at temperatures higher than 200 °C. By contrast, the methanation reaction could be avoided by using temperatures higher than 530 °C ($\Delta G > 0$). If methanation is avoided, it would prevent the loss of 3 mol of H₂ for each formed CH₄ [6].

In a recent work, Cavallaro et al. [7] investigated the support influence on the catalytic stability of several supported catalysts. They observed that Co/Al₂O₃ catalysts were deactivated after 2–3 h in the ethanol steam reforming (650 °C),

* Corresponding author. Tel.: +55-16-273-9945; fax: +55-16-273-9952.
E-mail address: edsont@iqsc.usp.br (E.A. Ticianelli).

and MgO represents a more suitable support for Co catalyst because of its lower acidity compared to Al₂O₃. The deactivation was attributed to cobalt oxidation and coke formation, but the amount of coke formed on the cobalt-support catalysts had not been quantified.

These results demonstrated that Co supported catalysts are more promising materials for hydrogen production by steam reforming of ethanol, but little is known about the mechanism of deactivation of these materials. In this work, Co/Al₂O₃, Co/SiO₂, and Co/MgO catalysts were prepared by an impregnation method involving a calcination step, and the materials were characterized by X-ray diffraction, atomic absorption spectroscopy, Raman spectroscopy, and temperature programmed reduction with hydrogen. After a reduction step, the catalytic performance of the materials was evaluated for steam reforming of ethanol at 400 °C. To characterize the deactivation mechanism, the amount of coke deposited after 9 h of reaction was determined by elemental analysis of carbon.

2. Experimental

The Co/ γ -Al₂O₃, Co/SiO₂ and Co/MgO catalysts were prepared by the incipient wetness impregnation of the γ -Al₂O₃ (Degussa), SiO₂ (Aerosil 200, Degussa) and MgO (Mallickrodt) supports, using an aqueous solution of Co(NO₃)₂·6H₂O (98%, Aldrich). The excess of water was removed in a rotative evaporator and the catalyst was dried and then calcined in air at 600 °C for 6 h.

The catalysts were characterized by X-ray diffraction (XRD), atomic absorption spectroscopy (AAS), Raman spectroscopy, temperature programmed reduction with hydrogen (H₂-TPR), and elemental analysis. The XRD analysis was performed to determine the bulk crystalline phases of cobalt species in the calcinated catalysts. XRD patterns were collected with a Rigaku-Miniflex diffractometer using monochromatized Cu K α radiation. The spectra were scanned from $2\theta = 20^\circ$ to 80° at a rate of $2^\circ/\text{min}$ (2θ). The measures of Raman spectroscopy were accomplished in a Renishaw spectrometer, operated at 0.070 mW. The spectra were collected between 150 and 850 cm^{-1} , using a helium–neon red laser (632.8 nm and diameter of 1 mm) with the sample exposed to air at ambient temperature. The quantification of the carbon deposited on the catalysts was accomplished by elemental analysis of C and H. These analyses used an Elemental Analyzers CE Instruments EA1110 CHNS-0, using 3 mg of catalyst in a tin capsule and the furnace temperature at 1200 °C. The H₂-TPR analyses were performed to determine the reduction behavior of the calcinated cobalt species on the different supports. These experiments were carried out in Micromeritics 2705 equipment, using 50 mg of catalyst and a temperature ramp from 25 to 1000 °C of $10^\circ\text{C}/\text{min}$. A flow rate of $30\text{ cm}^3/\text{min}$ of 5% H₂ in N₂ was used. 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 water produced during the reduction.

Catalytic performance tests were 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, four channels), which accurately control the flow of the gases (He, N₂, H₂, etc.) entering the reactor. The catalyst was placed in a quartz wool 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 of the pre-treatment and reaction steps. Prior to the reaction, 13 mg of the cobalt (80–167 mg of catalyst) was introduced into the reactor and reduced in situ in flowing H₂ ($40\text{ cm}^3/\text{min}$) at 650°C ($8^\circ\text{C}/\text{min}$) for 2 h, for activation of the catalyst. After this step, the sample was cooled down to 400°C under a pure N₂ flow. The reaction was started in a H₂-free environment feeding a 52% ethanol/water solution (1EtOH:3H₂O molar ratio) at a rate of $2\text{ cm}^3/\text{h}$. The liquid was pumped to a vaporizer, where the reagents were heated to 150°C and then fed to the reactor.

The analyses of the reactants and all the reaction 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 in 13X molecular sieve packed column, using helium as carrier gas. The other aliquot was used to analyze CO₂, CH₄, CO, C₂H₄, C₂H₅OC₂H₅, CH₃CHO, CH₃OCH₃, CH₃CO₂C₂H₅, C₂H₅OH, and H₂O. Nitrogen was used as a carrier gas and separation was accomplished by using a 13X molecular sieve and chromosorb (20% carbowax) packed columns. At the end of the catalytic test, the flow of ethanol/water was stopped and the catalyst was cooled under a He stream and stored for further characterization by elemental analysis.

3. Results and discussion

Table 1 shows the chemical composition of the cobalt-support catalysts, as obtained by AAS. The Co/MgO catalyst presents the largest content of cobalt while the Co/SiO₂ and Co/Al₂O₃ catalysts showed very close Co contents. Fig. 1 shows X-ray diffraction patterns for the Co/Al₂O₃, Co/SiO₂,

Table 1
Characteristics of the calcinated cobalt-supported catalysts

Catalysts	Co content (w/w%)	Co species
Co/Al ₂ O ₃	8.6	Co ₃ O ₄
Co/SiO ₂	7.8	Co ₃ O ₄
Co/MgO	18.0	Co ₃ O ₄

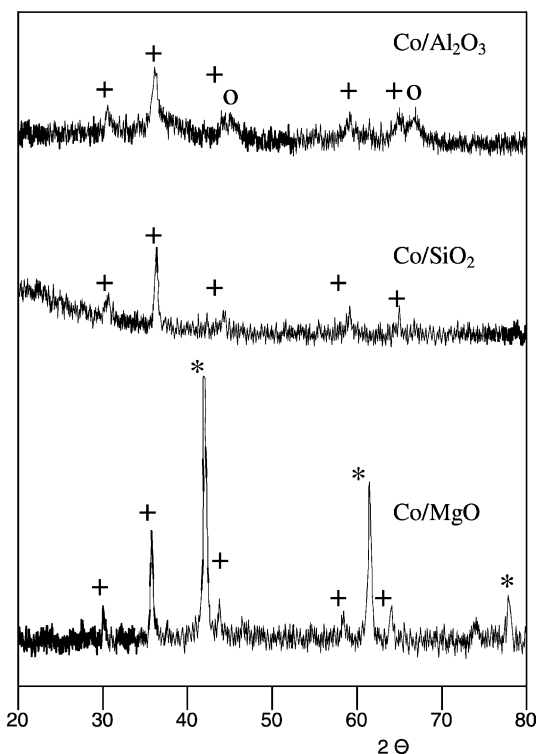


Fig. 1. X-ray diffraction patterns of Co/Al₂O₃, Co/SiO₂ and Co/MgO catalysts: (+) Co₃O₄; (*) MgO; (O) Al₂O₃.

and Co/MgO catalysts. For Co/Al₂O₃ and Co/SiO₂, the presence of the diffraction peaks centered at $2\theta = 32^\circ$, 37° , 45° , 59° , and 65° is indicative of the formation of Co₃O₄ (CoO \cdot xCo₂O₃) during the calcination step. The peaks at 47° and 68° for Co/Al₂O₃ and the peaks at 42° and 61° for Co/MgO are characteristic of the supports [8]. For Co/Al₂O₃ the diffraction peaks of Co₃O₄ are very close to that of CoAl₂O₄ ($2\theta = 31^\circ$, 37° , 65°). However, the presence of the low intensity peak at 45° observed for all supported Co catalysts, provide good evidence for assignment of the XRD features to Co₃O₄. The diffraction peaks at $2\theta = 37^\circ$ present the same intensity for Co/Al₂O₃ and Co/SiO₂, indicating that these catalysts have a similar Co loading. This is not the case for Co/MgO for which the intensity of this peak suggests higher Co loadings, as confirmed by the AAS analyses (Table 1).

Fig. 2 shows the Raman spectra obtained for all catalysts. It is noted that all spectra present bands centered at 197, 484, 524, 620, and 690 cm^{-1} , which are assigned to Co₃O₄. These results refer to the sample surface, but agree with the result for the material bulk, shown by XRD. In the case of Co/Al₂O₃, the absence of absorption bands centered at 410 and 750 cm^{-1} provides further evidence of the absence of cobalt aluminate, CoAl₂O₄ [9].

Results of the TPR-H₂ analyses of the calcinated Co/Al₂O₃, Co/SiO₂, and Co/MgO catalysts are presented in Fig. 3. All materials showed a reduction peak centered at 390°C , which is attributed to the reduction of Co₃O₄ to

metallic Co. The reduction peaks centered at 500°C (for Co/Al₂O₃ and Co/MgO) and 650°C (only for Co/Al₂O₃) correspond to the reduction of CoO_x to metallic Co, for a system with strong cobalt-support interaction. These peaks are absent for Co/SiO₂, showing that there is no interaction of the Co-species with this support. On the contrary, for Co/Al₂O₃, the presence of the peak at 650°C resulting from a more difficult reduction process indicates that the cobalt-support interactions are very high.

In initial experiments, it was observed that oxidized cobalt species (CoO \cdot xCo₂O₃) are not active for the steam reforming of ethanol. It was also seen that after the catalyst reduction (650°C , 2 h under H₂), all materials gave an ethanol conversion of more of 90%. The on-line analysis of the products had shown formation of acetaldehyde, ethyl ether, acetone, and ethyl acetate. However, the sum of the contributions of all these products was less than 1%. Because of the long time of the experiments and the small amount of liquid product, the reaction effluents were condensed in order to improve the accuracy of the analyses of the gaseous products.

Fig. 4 shows the distribution of the gaseous products as a function of time, for the steam reforming of ethanol on the reduced Co-based catalysts at 400°C . It is seen that hydrogen production rises rapidly in the beginning of the experiments, until a plateau near 70% is reached. The hydrogen yield is close to the value observed by Haga et al. [6] (67%) and the H₂/EtOH ratio near to 5 is close to that expected from thermodynamic equilibrium, also agreeing with the results of Cavallaro et al. [7]. Besides hydrogen, the formation of CO, CO₂, and CH₄ is observed, with relative amounts depending on the catalyst substrate. For Co/Al₂O₃, ethene was also observed as a reaction product (10–18%), and this is the result of the ethanol dehydration promoted by the acid sites of alumina. The Co/SiO₂ and Co/Al₂O₃ catalysts produced amounts of CO of about 3–8%, while for Co/MgO the amount was 14%. The amount of CO observed here is in agreement with those observed in the process of alcohol steam reforming (1–14%) [2]. In general, the catalysts gave a CO₂/CO_x ratio in the range of 30–50%, which was larger for the Co/SiO₂ catalyst. However, the Co/SiO₂ catalyst produced a higher amount of methane, compared to the other catalysts (~18%).

It has been proposed that the formation of methane on Co/MgO and Cu/SiO₂ catalysts occurs via a methanation of CO (reaction 4), that is:



while on Co/Al₂O₃, methane is produced by ethanol decomposition [6]. It is also known that above 530°C the methanation reaction stops because the ΔG° of reaction 4 becomes positive, while the rate of ethanol decomposition always increases with the increase of temperature. Thus, an attempt to minimize methane formation *via* the methanation of CO was made for the Co/SiO₂ catalyst by conducting the reforming reaction at 550°C . Table 2 compares the product distributions at 400 and 550°C , after 4 h of reaction. A small

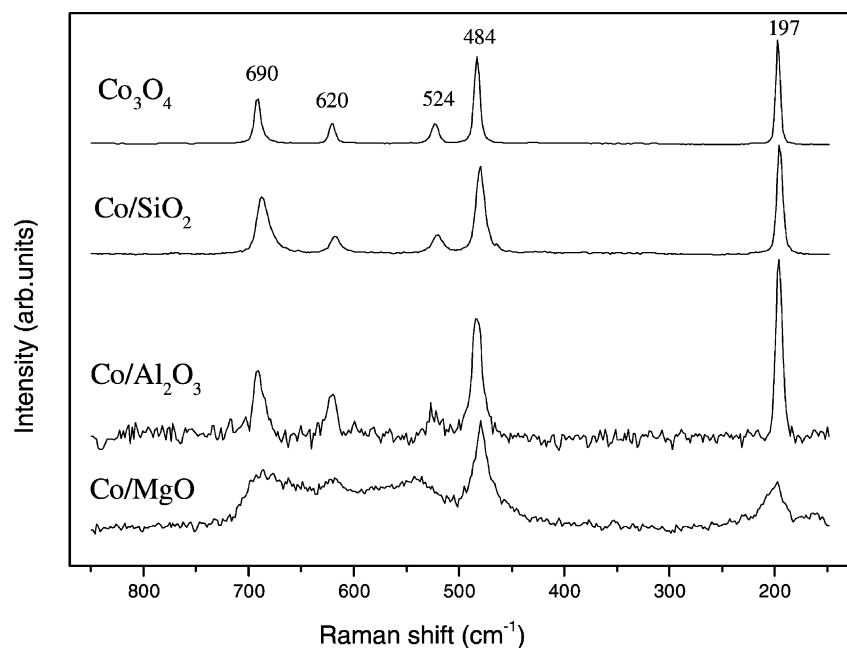


Fig. 2. Raman spectra of cobalt-support catalysts and Co_3O_4 .

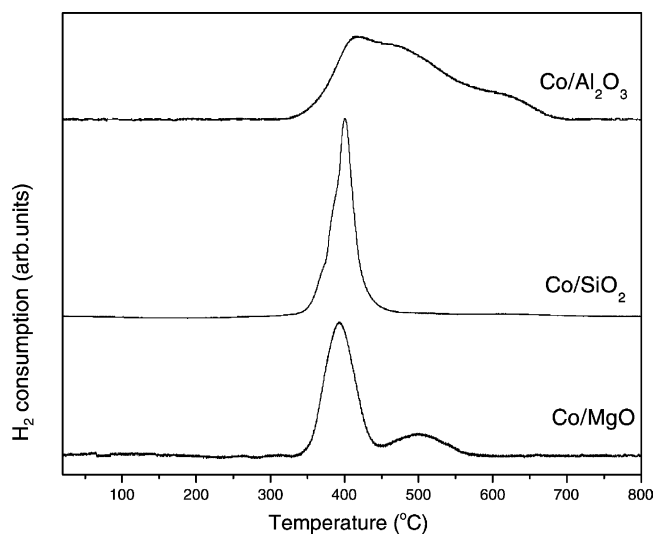


Fig. 3. H_2 -TPR profiles of cobalt-support catalysts.

Table 2

Results of steam reforming of ethanol on the Co/SiO_2 catalyst at 400 and 550 °C after 4 h

Product	Composition (mol%)	
	400 °C	550 °C
H_2	74.0	71.0
CO_2	3.8	1.6
CH_4	18.3	16.0
CO	3.9	11.4

Table 3

Coke formation on the cobalt-support catalysts, after 9 h of steam reforming reaction at 400 °C

Catalysts	Amount of carbon (w/w%)
$\text{Co/Al}_2\text{O}_3$	24.6
Co/SiO_2	14.2
Co/MgO	17.0

reduction in the formation of H_2 , CO_2 , and CH_4 is observed at 550 °C, while the opposite occurs for CO . The decrease of CH_4 formation is much less than that expected from the ΔG changes of reaction 4, probably because the methanation of CO is not an important pathway for CH_4 formation, in contrast of what proposed in previous investigations. The present results indicate that the decomposition of ethanol determines the CH_4 formation for all catalyst supports.

A clear decrease in the efficiency of ethanol reforming is observed from results of experiments running up to 9 h. After this time, the $\text{Co/Al}_2\text{O}_3$, Co/SiO_2 , and Co/MgO catalysts were analyzed in order to evaluate the amount of deposited carbon. Table 3 shows these results, expressed in terms of the weight percent (wt.%) of carbon with respect to the total weight of the sample. It is seen that a considerable amount of carbon is formed, the largest being for the $\text{Co/Al}_2\text{O}_3$ catalyst. In this case, it is proposed that the acid sites of alumina may promote the cracking of the ethanol molecules, besides the dehydration path forming ethene.

Fierro et al. [10] observed that about 20–90 mg/(h g_{catalyst}) of carbon are deposited on Ni-Cu/SiO_2 catalyst during the ethanol steam reforming at 600 °C. If this result is

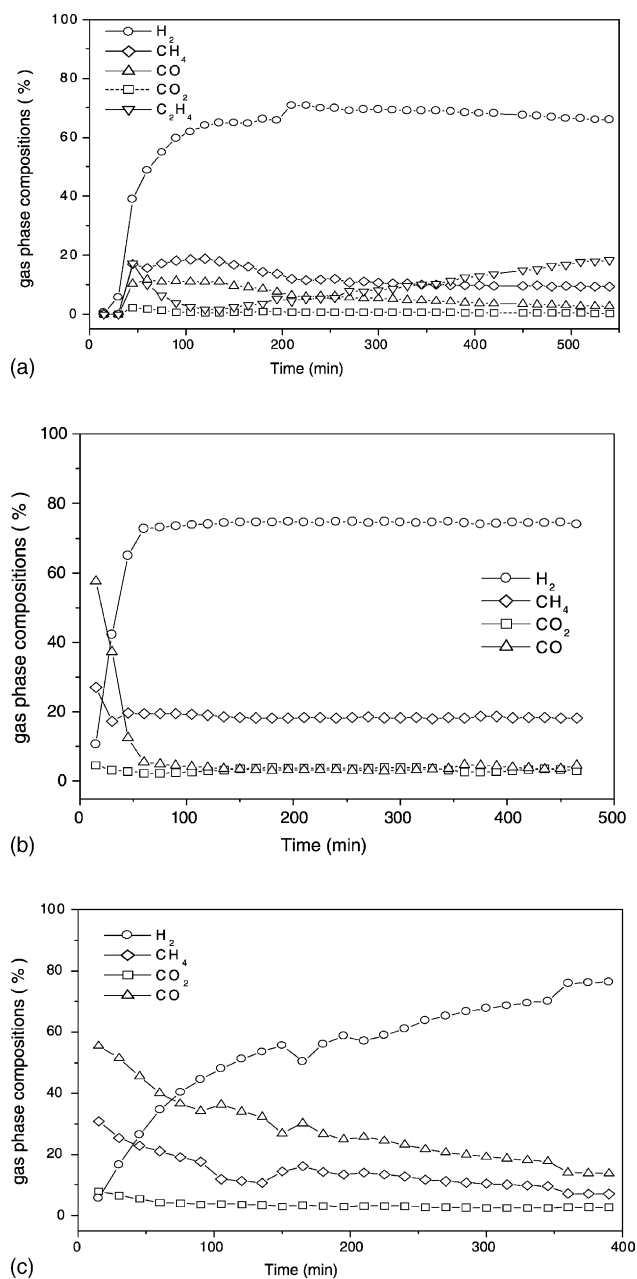


Fig. 4. Gas phase composition of the reaction product on the several catalysts: (a) Co/Al₂O₃; (b) Co/SiO₂; and (c) Co/MgO.

compared with those obtained with the Co/Al₂O₃ catalyst, it is observed that the amount of deposited coke is much smaller (0.02 mg/(h g_{catalyst})). In any case, the amount of coke deposited on the cobalt-supported catalysts is enough to provide an accentuated fall in the catalytic activity after 9 h of reaction. Independent of the carbon amount, the present experiments had shown that coke formation is the main reason for the catalyst performance decay, as observed for all catalysts.

4. Conclusions

XRD and Raman analyses of the Co/Al₂O₃, Co/SiO₂, and Co/MgO catalysts, prepared by the impregnation method and calcinated at 600 °C had indicated formation of Co₃O₄ (Co xCo₂O₃) as the main constituent of the Co phase. For Co/Al₂O₃ and Co/MgO, TPR-H₂ analyses had shown the presence of some interaction between the CoO_x species and the support, this being stronger for Co/Al₂O₃, as indicated by the higher reduction temperature of the Co species.

High conversion levels (>90%) were seen for the steam reforming of ethanol in all catalysts. These results also show that metallic Co is the active center for the catalytic process. Hydrogen is the main constituent of the reaction effluent, which also contains CO, CO₂, and CH₄. In the case of Co/Al₂O₃ a significant amount of ethylene was detected in the gaseous stream, and this was formed by dehydration of ethanol at the acid sites of alumina. Co/SiO₂ gave the highest quantity of methane and Co/MgO the highest amount of CO. The present results indicate that the decomposition of ethanol determines the CH₄ formation for all catalysts.

A considerable amount of carbon is deposited in all catalysts after 8–9 h of reaction, the largest being for Co/Al₂O₃ for which the acid sites of alumina may promote the cracking of the ethanol molecules. The present experiments have also shown that coke formation is the main reason for the catalyst performance decay during long time operation inside a steam reforming reactor.

Acknowledgements

The authors wish to thank Fundação de Amparo a Pesquisa do Estado de São Paulo for financial assistances.

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