CHEMICAL ENGINEERING TRANSACTIONS

VOL. 37, 2014

A publication of
AIDIC
The Italian Association
of Chemical Engineering
www.aidic.it/cet

Guest Editors: Eliseo Ranzi, Katharina Kohse- Höinghaus

**ISBN** 978-88-95608-28-0; **ISSN** 2283-9216

DOI: 10.3303/CET1437081

# Analysis of Ni/$La_2O_3$–α$Al_2O_3$ Catalyst Deactivation by Coke Deposition in the Ethanol Steam Reforming

Carolina Montero*, Beatriz Valle, Javier Bilbao, Ana G.Gayubo

Chemical Engineering Department. University of the Basque Country UPV/EHU.P.O.Box.644,48080. Bilbao-Spain.
carodrmontero@gmail.com

The effect of C-containing byproducts on the deactivation of Ni/$La_2O_3$-α$Al_2O_3$ catalyst in the steam reforming of ethanol (SRE) was studied. The catalyst was prepared by wet impregnation method and subsequently calcined at 550ºC and reduced at 700ºC, prior the reforming reactions. The kinetic runs were carried out in a fluidized bed reactor under the following operating conditions: atmospheric pressure; 500 ºC; space-time, 5.2 and 9.2 $g_{catalyst}$ min $g_{EtOH}^{-1}$ and time on stream, 20 h. The properties of the fresh and used catalysts were analyzed by $N_2$ adsorption-desorption, $H_2$ chemisorption and X-ray diffraction (XRD), and the nature and amount of coke deposited on the catalyst were analyzed by Scanning Electron Microscopy (SEM) and Temperature Programmed Oxidation (TPO) analysis. It was found that the catalyst deactivation level is not directly dependent on the coke content but it highly depends on ethanol conversion: for a low conversion, the coke deposited encapsulates and blocks the metallic active sites, causing a fast deactivation of the catalyst, whereas for a high conversion the coke is deposited as filamentous carbon that contributes to decreasing the catalyst porosity but without affecting notably to catalyst stability. The different nature of the coke deposited on the catalyst is attributed to the intermediate compounds produced in the reaction medium, with acetaldehyde being the major responsible for the formation of encapsulating coke, whereas the $CH_4$ and CO presence favors the formation of fibrous coke.

## 1. Introduction

The global population growth, the decrease in oil sources and the tightening of environmental legislation drive the search of new alternative sources for supplying technologically and economically feasible energy. Lignocellulosic biomass (mainly composed of C, H and O) can be converted by thermal or bio-chemical techniques into organic compounds with higher calorific value per mass unit. Among these, the production of bio-ethanol by sugar fermentation is favored by the rapid technological development of the enzymatic hydrolysis step (Menon and Rao, 2012, Ensinas et al, 2013). Besides, the production of high added-value products derived from bio-ethanol is interesting to make profitable the biomass valorization.

The steam reforming of bio-ethanol is an interesting route for the sustainable production of hydrogen, whose current demand is growing due to its use in agriculture, food and metallurgical industries and especially due to its interest as a fuel and petrochemical raw material. Nowadays, hydrogen is obtained by steam reforming of natural gas and oil naphtha fractions (Balat and Kirtay, 2010). The catalytic steam reforming of ethanol (SRE) avoids the costly dehydration steps required for other valorization strategies and contributes to the development of the bio-refinery concept. It is a highly endothermic process that proceeds according to the overall equation:

$$C_2H_6O + 3\ H_2O \rightarrow 2\ CO_2 + 6\ H_2 \qquad (1)$$

Based on results of temperature effect on product distribution (Vaidya and Rodrigues, 2006) and sensitive spectroscopic methods (Sánchez-Sánchez et al., 2010), the dissociative adsorption of ethanol as *ethoxy* species followed by dehydrogenation to acetaldehyde has been established as the main reaction pathway. Furthermore, there may be parallel reactions that decrease the $H_2$ yield and originate the presence of byproducts in the reaction medium, such as, dehydration of ethanol to ethylene, decomposition of acetaldehyde to CO and $CH_4$, Eq(2), and methanation of $CO_2$ and CO, Eq(3):

Please cite this article as: Montero C., Valle B., Bilbao J., Gayubo A., 2014, Analysis of ni/la2o3–αal2o3 catalyst deactivation by coke deposition in the ethanol steam reforming, Chemical Engineering Transactions, 37, 481-486 DOI: 10.3303/CET1437081

$CH_3CHO \rightarrow CO + CH_4$ (2)

$CO + 3H_2 \leftrightarrow CH_4 + H_2O$ (3)

On the other hand, the $H_2$ yield may be increased by reactions such as the Water Gas Shift (WGS), Eq(4), and the reforming of $CH_4$. Additionally, there are undesired reactions that contribute to catalyst deactivation by coke formation, such as the Boudouard reaction and the dehydrogenation of $CH_4$:

$CO + H_2O \leftrightarrow CO_2 + H_2$ (4)

$2CO \leftrightarrow C + CO_2$ (5)

$CH_4 \rightarrow C+2H_2$ (6)

The studies in the literature have focused on obtaining a catalyst that maximizes the hydrogen yield and minimizes the coke formation. Noble (Pt, Pd, Rh, Ru, Au) and non-noble (Ni, Co, Cu) metal based catalysts, deposited on different supports, have been extensively studied (Palma et al, 2014). Regarding these, the Ni-based catalysts are relatively cheap and easy to regenerate and reuse (Nahar and Dupont, 2012) and $Al_2O_3$-based supports are often used due to its mechanical and chemical resistance. Sánchez-Sánchez et al (2007) studied the effect of La, Mg, Zr and Ce oxides addition, reporting that the presence of La and Ce prevent the formation of carbon filaments. Alberton et al. (2007) found that the NiO activity over $\alpha$-$Al_2O_3$ is much higher than over $\gamma$-$Al_2O_3$, due to the migration of Ni particles on carbon filaments.

In this paper, a study was carried out on the deactivation by coke deposition of a $Ni/La_2O_3$-$\alpha Al_2O_3$ catalyst in the steam reforming of ethanol by analyzing the effect of space-time and composition of the product stream on the nature and amount of the coke deposited, in order to determinate the coke precursors and relationship between coke nature and catalyst deactivation.

## 2. Experimental

### 2.1 Synthesis and characterization of the catalyst

The $Ni/La_2O_3$-$\alpha Al_2O_3$ (with 10 wt% Ni and 9 wt% $La_2O_3$ nominal contents) was prepared by incipient wetness impregnation method. The $\alpha Al_2O_3$ support was modified with $La_2O_3$ by impregnation with an aqueous solution of $La(NO_3)_3 \cdot 6H_2O$, under vacuum at 70 ºC. The modified support was then dried at 100 ºC for 24 h and calcined at 900 ºC for 3 h. Subsequently, Ni was impregnated by Ni $(NO_3)_2 \cdot 6H_2O$ solution, dried at 110 ºC for 24 h and finally calcined for 2 h at 550 ºC (Valle et al, 2014).

Prior to reforming reactions, the catalyst was equilibrated with (steam reforming)-regeneration cycles under the following conditions: i) Reduction *in-situ* at 700 °C for 2 h by using $H_2$–He flow (10 %v/v $H_2$); ii) Steam reforming with decreasing temperature steps (700-600-500 ºC, 2 h at each temperature), space-time ($W/F_0$) = 20.4 $g_{catalyst}$ min $g_{EtOH}^{-1}$ and steam/ethanol molar ratio (S/E) = 3, iii) Regeneration by combustion with air (150 ml/min) at 550 ºC for 2 h.

The physical properties of fresh and deactivated catalyst (BET surface area and pore volume) were analyzed by $N_2$ adsorption-desorption (Quantachrome $IQ_2$ analyzer-physisorption mode). The Ni dispersion and the specific metal surface were determined by $H_2$ chemisorption (Quantachrome $IQ_2$ analyzer-chemisorption mode). The Ni content was measured by inductively coupled plasma quadrupole mass spectroscopy (Q-ICP-MS Thermo X7-II). The average $Ni^0$ particle size was calculated by applying the Scherer's formula to the peak at $2\theta = 52º$ of the X-ray diffraction (XRD) analysis (difractometer PHILIPS X´PERT PRO).

The coke content was determined by temperature programmed oxidation (TPO) in a thermobalance (Q5000 IR TA Instruments) connected on-line to a mass spectrometer for monitoring the signal corresponding to $CO_2$. Coke morphology was analyzed by Scanning Electron Microscope (SEM) (JEOL/JSM-7000).

### 2.2 Reaction equipment and operating conditions

The experiments were performed in automated reaction equipment (Figure 1) provided with an isothermal fluidized-bed reactor connected on-line to a gas chromatograph (Agilent µGC 3000) for product analysis. The µGC has four analytical modules with TCD detector for the quantification of the following products: 1) *5A molecular sieve*: $O_2$, $N_2$, $H_2$, CO, $CH_4$; 2) *plot Q*: $CO_2$, $H_2O$; 3) *alumina*: $C_2$-$C_4$; 4) *stabylwax*: acetaldehyde, acetone and ethanol.

The reforming conditions were: 500°C, atmospheric pressure, steam-to-ethanol molar ratio (S/E) = 6.3 (suitable for maximizing the $H_2$ yield and minimizing the coke formation (Alberton et al., 2007)), space-time

$(W/F_0)$ = 5.2 and 9.2 $g_{catalyst}$ min $g_{EtOH}^{-1}$; time-on-stream, 20 h. In order to assure that carbon deposition is not affected by the hydrodynamics conditions, the same ratio (gas velocity)/(minimum fluidization velocity) is used for both values of space-time. The hydrodynamic properties of the bed are improved by mixing the catalyst (particle size 0.15-0.25 mm) with an inert solid (CSi, 37 μm) (Remiro, 2012).

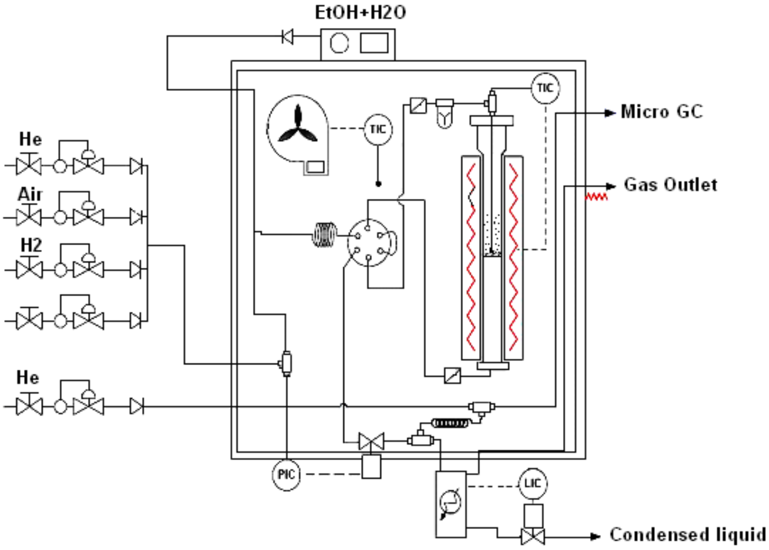

*Figure 1: Scheme of reaction equipment for the steam reforming of ethanol.*

### 2.3 Reaction indices

The conversion of ethanol is calculated from its molar flow-rate at the inlet and outlet (un-reacted ethanol) of the catalytic reactor, according to:

$$X_{EtOH} = \frac{F_{EtOH,inlet} - F_{EtOH,outlet}}{F_{EtOH,inlet}} \tag{7}$$

The $H_2$ yield is calculated as a fraction of the stoichiometric potential of the feed, corresponding to complete conversion of the carbon contained in the ethanol to $CO_2$, according to Eq(1):

$$Y_{H2} = \frac{molar\ flow\ of\ H_2\ obtained}{(6xF_{EtOH,inlet})} \tag{8}$$

The yield of each carbon-containing byproduct (CO, $CO_2$, $CH_4$, ethylene, acetaldehyde,…) is quantified by:

$$Y_i = \frac{molar\ flow\ of\ i\ (CO,CO_2,CH_4,HC\ldots)\ obtained}{(2xF_{EtOH,inlet})} \tag{9}$$

## 3. Results and Discussion

The effect of space-time on ethanol conversion and products distribution and on catalyst deactivation rate is observed in Figure 2, which shows the evolution with time on stream of ethanol conversion and $H_2$ yield (Figure 2a) and the yields of CO, $CH_4$ and acetaldehyde (Figure 2b) as reaction by-products. The $CO_2$ yield is not shown as it has a similar trend to $H_2$ yield, and only incipient quantities of light hydrocarbons (ethane and ethylene) are formed under these operating conditions.

A significant increase in ethanol conversion and $H_2$ yield at zero time on stream is observed by increasing the space-time, with ethanol being fully converted at 9.2 $g_{catalyst}$ min $g_{EtOH}^{-1}$ with $H_2$ yield of around 0.50, which is almost steady throughout 8 h reaction (Figure 2a). For this value of space-time, the $CH_4$ yield is high (≈ 0.3) and decreases slightly in 20 h reaction (Figure 2b), whereas the CO yield increases with time on stream and a negligible amount of acetaldehyde is obtained. These results suggest that under these conditions, ethanol dehydrogenates to form acetaldehyde, which is fully decomposed into $CH_4$ and CO, Eq(2). Moreover, at 500 ºC both CO methanation, Eq(3), and WGS reaction, Eq(4), are enhanced, thus causing the higher yield of $CH_4$ with respect to CO. The deactivation of these reactions with time on stream causes the increase in CO yield, the decrease in $CH_4$ yield (Figure 2b) and the slight decrease in $H_2$ yield (Figure 2a).

For $W/F_0$ = 5.2 $g_{catalyst}$ min $g_{EtOH}^{-1}$ the values at zero time on stream of ethanol conversion and $H_2$ yield are low, around 0.58 and 0.10, respectively, and they decrease rapidly to 0.20 and 0.02 in 3 h, with these values remaining steady until the end of reaction. For this low value of space-time, the mayor C-containing by-product is acetaldehyde (Figure 2b) with an initial value of 0.30 that decreases to 0.08 in 3 h and negligible amounts of CO and $CH_4$ are obtained. Under these conditions, the main reaction pathway for ethanol conversion is dehydrogenation to form acetaldehyde, which is rapidly deactivated in 2 h reaction (Figure 2b). The ethanol reforming activity at this low value of space-time is significantly lower than that observed at 9.2 $g_{catalyst}$ min $g_{EtOH}^{-1}$, thus obtaining markedly lower $H_2$ yield (Figure 2a). It should be mentioned that the C-balance for both space-time values are close to 99.8%.

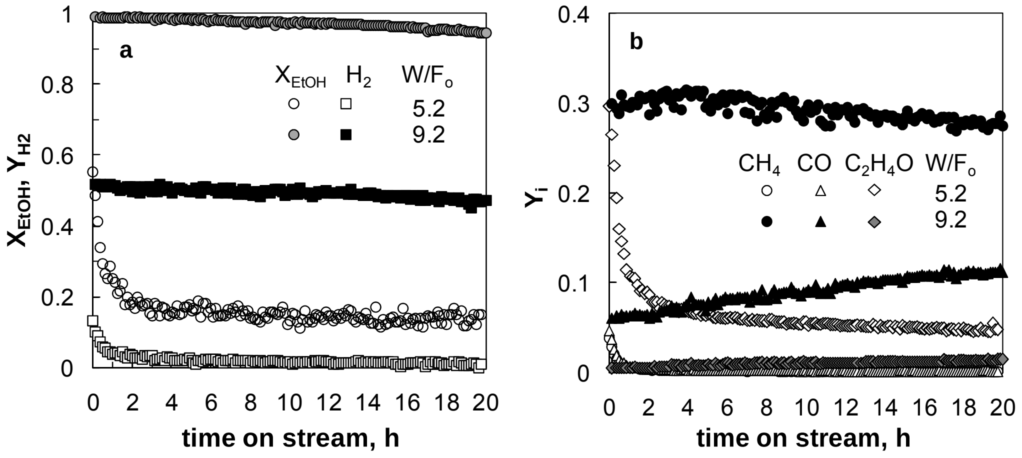

*Figure 2: Evolution with time on stream of (a) ethanol conversion and hydrogen yield and (b) yields of $CH_4$, CO and acetaldehyde. Conditions: 500°C, S/E=6.28, $W/F_0$ = 5.2 and 9.2 $g_{catalyst}$ min $g_{EtOH}^{-1}$.*

Table 1 shows the metallic properties of the fresh $Ni/La_2O_3$-$\alpha Al_2O_3$ catalyst, whereas the physical properties of the fresh catalyst and those of the catalyst used in SRE at 500 ºC for different values of space-time, along with the corresponding coke contents are shown in Table 2..

*Table 1: Metallic properties of fresh $Ni/La_2O_3$-$\alpha Al_2O_3$ catalyst*

| Ni content, % | La content, % | $Ni^0$ size, nm | $Ni^0$ dispersion, % |
|---|---|---|---|
| 8.82 | 6.79 | 10.6 | 4.05 |

*Table 2: Physical properties of the fresh and used (at 500 ºC) $Ni/La_2O_3$-$\alpha Al_2O_3$ catalyst*

| Catalyst | $S_{BET}$, $m^2/g$ | Pore volume, $cm^3/g$ | $d_{pore}$, A° | Coke, wt% |
|---|---|---|---|---|
| Fresh | 35.25 | 0.179 | 61.76 | -- |
| Used ($W/F_0$ = 5.2 $g_{catalyst}$ min$g_{EtOH}^{-1}$) | 35.12 | 0.198 | 61.86 | 1.1 |
| Used ($W/F_0$ = 9.2 $g_{catalyst}$ min$g_{EtOH}^{-1}$) | 156.65 | 0.159 | 19.13 | 48.8 |

It can be noted that the physical properties of the fresh catalyst and of the catalyst used with a low value of space-time (5.2 $g_{catalyst}$ min $g_{EtOH}^{-1}$) are very similar, as it could be expected from the low value of coke deposited under these conditions (1.1 wt%), which is in accordance with previous results in literature (1.48 wt % for a space-time ≈ 5 $g_{catalyst}$ min $g_{EtOH}^{-1}$ and S/E =3, reported by Sánchez-Sánchez et **al (2007).** Nevertheless, the catalyst used with a high value of space-time has a noticeably higher value of BET surface area and lower value of pore volume and pore size that the fresh catalyst. This fact should be attributed to a high deposition of coke (48.8 wt%) with porous structure, as that corresponding to a filamentous coke. The decrease in pore diameter observed for this used catalyst could be caused by the partial coverage of the porous structure of the support by highly developed carbon filaments.

The results in Figure 2 and Table 2 clearly shows that under conditions of high ethanol conversion (high space-time), the catalyst deactivation is low although the coke deposition is high, whereas for low conversion of ethanol (low space-time) the opposite occurs. This result indicates that the deactivation rate is not directly affected by the coke content, thus suggesting that the nature of the coke deposited must be the responsible for the catalyst deactivation rate.

The results of coke nature characterization by TPO analysis and SEM images are shown in Figures 3 and 4, respectively. The TPO profile of the coke deposited under conditions of low ethanol conversion (low space-time) shows a combustion peak at low temperature (≈ 350 °C) which evidences the presence of amorphous coke (monatomic and polymeric, whose combustion is activated by the metal) that is adsorbed on the metal sites and cover them (encapsulating coke), thus causing a rapid deactivation (Bartholomew, 2001). Under conditions of high ethanol conversion, there is a combustion peak at high temperature (550 °C) which corresponds to a filamentous coke with different graphitization degree (Sánchez-Sánchez et al., 2007; He et al., 2012), which does not blocks metal sites and, consequently has a lower effect on catalyst deactivation. The SEM images of the coke samples reveal the fibrous structure of the coke deposited at 9.2 $g_{catalyst}$ min $g_{EtOH}^{-1}$ (Figure 4b).

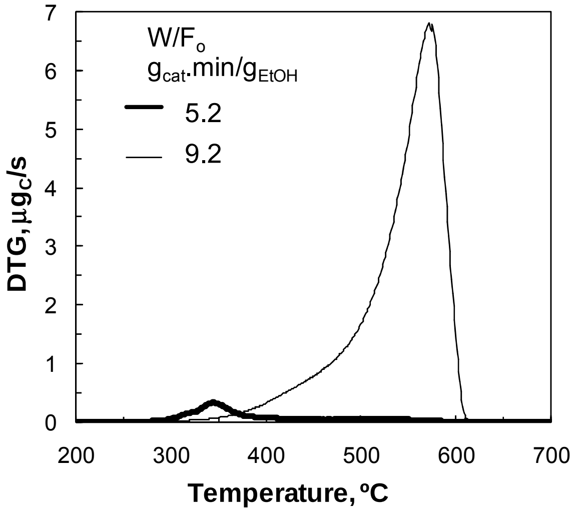

*Figure 3: Results of TPO analysis of coke deposited on $Ni/La_2O_3$–$\alpha Al_2O_3$ catalyst in SRE at 500 °C, S/E=6.28, space-time ($W/F_0$) = 5.2 and 9.2 $g_{catalyst}$ min $g_{EtOH}^{-1}$.*

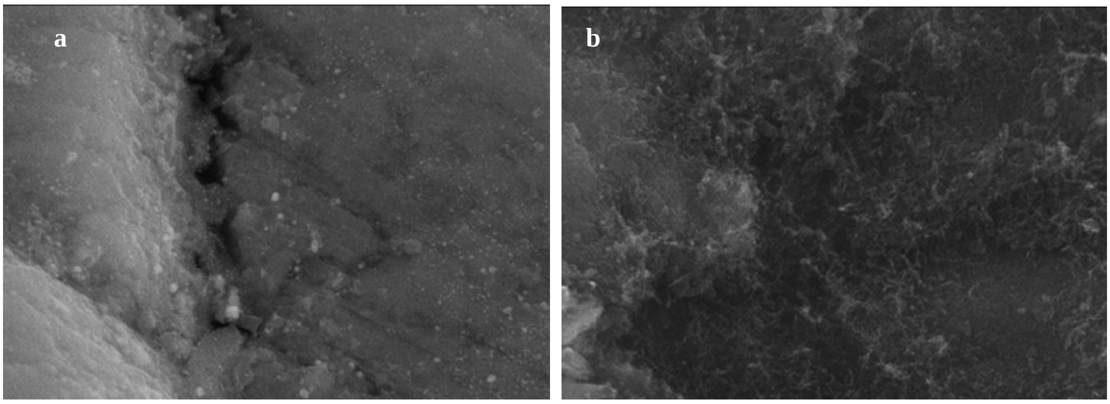

*Figure 4: SEM images of coke deposited on $Ni/La_2O_3$–$\alpha Al_2O_3$ catalyst in SRE at 500 °C, S/E=6.28, and space-time: a) 5.2 and b) 9.2 $g_{catalyst}$ min $g_{EtOH}^{-1}$.*

Based on the above results, the origin of encapsulating coke must be acetaldehyde, which is the main product obtained under the conditions that enhance the formation of this type of coke (low space-time). The filamentous coke precursors must be $CH_4$ (through decomposition reaction) and CO (through Boudouard reaction), which are the main by-products when ethanol conversion is high.

## 4. Conclusions

It has been found that the nature of the coke is the factor controlling the Ni/$La_2O_3$-α$Al_2O_3$ catalyst deactivation degree in the steam reforming of ethanol at 500 °C, whereas the amount of coke deposited does not have a direct relationship with catalyst deactivation. The encapsulating coke (monatomic and polymeric coke with TPO peaks below 450 °C) adsorbed on the metal is the main responsible for the catalyst deactivation by blocking of metal sites, whereas the fibrous coke (with TPO peaks above 500 °C), consisting of filamentous carbon, has less influence on deactivation.

The nature of the coke deposited depends on the composition of the reaction medium. $CH_4$ and CO (whose concentration is high for high values of space-time (full conversion of ethanol)) favor the development of coke filaments or fibers, thus resulting in low deactivaction althoguh the coke content is high under these conditions. On the contrary, acetaldehyde (whose presence in the reaction medium is high for low values of space-time) promotes the formation of encapsulating coke and, therefore, a noticeable deactivation of the catalyst, even though for very low values of coke content

Consequently, the Ni/$La_2O_3$-α$Al_2O_3$ catalyst has an interesting behavior in SRE at 500 °C and high values of space-time (above) 9.2 $g_{catalyst}$ min $g_{EtOH}^{-1}$, since the filamentous coke formation is favored, which minimizes catalyst deactivation by Ni sites blockage.

### Acknowledgements

This work has been carried out with the financial support of The National Secretariat of Higher Education, Science, Technology and Innovation of Ecuador SENESCYT (Contract 20110560) and the Ministry of Science & Technology of the Spanish Government (Projects CQT2009-13428 and CTQ2012-35263).

### References

Alberton A.L., Souza M.M.V.M., Schmal M., 2007, Carbon formation and its influence on ethanol steam reforming over Ni/$Al_2O_3$ catalysts, Catalysis Today, 123, 1–4, 257-264.

Balat H., Kırtay E., 2010, Hydrogen from biomass-Present scenario and future prospects, International Journal of Hydrogen Energy, 35, 14, 7416-7426.

Bartholomew C.H., 2001, Mechanisms of catalyst deactivation, Applied Catalysis A:General, 212 17-60.

Ensinas A.V., Codina V., Marechal F., Albarelli J., Silva M.A., 2013, Thermo-economic optimization of integrated first and second generation sugarcane ethanol plant, Chemical Engineering Transactions, 35, 523-528.

He Z., Yang M., Wang X., Zhao Z., Duan A., 2012, Effect of the transition metal oxide supports on hydrogen production from bio-ethanol reforming, Catalysis Today, 194, 2-8.

Menon V., Rao M., 2012, Trends in bioconversion of lignocellulose: Biofuels, platform chemicals & biorefinery concept, Progress in Energy and Combustion Science, 38, 522-550.

Nahar G., Dupont V., 2012, Hydrogen via steam reforming of liquid biofeedstock, Biofuels, 3, 167-191.

Palma V., Castaldo F., Ciambelli P., Iaquaniello G., 2014, $CeO_2$-supported Pt/Ni catalyst for the renewable and clean $H_2$ production via ethanol steam reforming, Applied Catalysis B: Environmental, 145, 73-84.

Remiro A., Valle B., Aguayo AT., Bilbao J., Gayubo A.G., 2013, Operating conditions for attenuating Ni/$La_2O_3$–α$Al_2O_3$ catalyst deactivation in the steam reforming of bio-oil aqueous fraction, Fuel Processing Technology, 115, 222-232.

Remiro A., 2012, Hydrogen production by steam reforming of bio-oil: Integration of thermal, catalytic and $CO_2$ capture steps in the process. Ph.D. Thesis, University of the Basque Country, Bilbao, Spain.

Sánchez-Sánchez M.C., Yerga R.M.N., Konkarides D.I., Verykios X.E., Fierro J.L.G, 2010, Mechanistic aspects of the ethanol steam reforming reaction for hydrogen production on Pt, Ni, and PtNi catalysts supported on γ-$Al_2O_3$, Journal of Physical Chemistry A,114, 3873-3882.

Sánchez-Sánchez M.C., Navarro R.M., Fierro J.L.G., 2007, Ethanol steam reforming over Ni/$M_xO_y$-$Al_2O_3$ (M=Ce, La, Zr and Mg) catalysts: Influence of support on the hydrogen production, International Journal of Hydrogen Energy, 32, 10–11, 1462-1471.

Vaidya P.D. ,Rodrigues A.E., 2006, Kinetics of steam reforming of ethanol over a Ru/$Al_2O_3$ catalyst, Industrial and Engineering Chemistry Research, 45, 19, 6614-6618.

Valle B., Aramburu B., Remiro A., Bilbao J. Gayubo A.G., 2014, Effect of calcination/reduction conditions of Ni/$La_2O_3$–α$Al_2O_3$ catalyst on its activity and stability for hydrogen production by steam reforming of raw bio-oil/ethanol, Applied Catalysis B: Environmental, 147, 402-410.