Decomposition of ethanol over Ni-Al catalysts: effect of copper addition

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Abstract

A series of Ni-Al hydrotalcite-type samples modified with copper was prepared and evaluated for use in the decomposition of ethanol. The partial substitution of Ni by Cu has small influence on the specific surface area and on the structure (XRD). However, it has a strong influence on the degree of reducibility (shifts to lower temperatures) and on the selectivity of reaction. The selectivity towards H₂ and CO increases for reactions conducted at a higher temperature, which is followed by a decrease in the amount of carbon formed. Catalysts with a high Cu content exhibit lower selectivity for H₂ and CO. SEM images show that carbon nanotubes with greater and more variable diameters and lengths were formed by Cu-loaded catalysts, possibly due to the sintering of copper. Nevertheless, the Raman spectra suggest that the nanotubes produced by the Cu-containing samples have higher purities and fewer defects.

Keywords: Decomposition of ethanol; Ni-based catalysts; hydrotalcite-type materials; carbon nanotubes; copper

1. Introduction

In the search for alternative fuels, catalytic processes that produce hydrogen and synthesis gas have attracted great attention. Aside from involving a renewable biomass resource, the decomposition of
ethanol can generate ethylene, \( \text{H}_2 \) and synthesis gas (\( \text{H}_2 \) and CO), depending on the process operation conditions and the catalyst used. Furthermore, ethanol can be used as a carbon source in the synthesis of carbon nanotubes (CNT) that have outstanding physical and chemical properties.

In this process, the primary reactions that take place are the decomposition of ethanol to light gases (eq. 1) and the dehydration of ethanol (eq. 2). Additionally, the methane produced in eq. 1 can be further decomposed to hydrogen and carbon (eq. 3), increasing the \( \text{H}_2 \) yield and providing a more suitable \( \text{H}_2/\text{CO} \) molar ratio for Fischer-Tropsch synthesis.

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\begin{align*}
\text{C}_2\text{H}_5\text{OH} & \rightarrow \text{CH}_4 + \text{CO} + \text{H}_2 \quad \Delta H_{298K} = 49 \text{ kJ mol}^{-1} \\
\text{C}_2\text{H}_5\text{OH} & \rightarrow \text{C}_2\text{H}_4 + \text{H}_2\text{O} \quad \Delta H_{298K} = 45 \text{ kJ mol}^{-1} \quad (2) \\
\text{CH}_4 & \rightarrow \text{C} + 2\text{H}_2 \quad \Delta H_{298K} = 75 \text{ kJ mol}^{-1} \quad (3)
\end{align*}
\]

Recently, Ni-based catalysts used in this process have shown promising results [1-3]. Investigations of hydrotalcite-type (HT) nickel catalysts have exhibited very interesting properties and performances in other reactions involving ethanol [4, 5]; however, results regarding the carbon formed over these materials are scarce. Copper can modify the reduction profiles of samples [6, 7] and could possibly improve their performance in the decomposition of ethanol. Therefore, we herein investigate HT Ni-Al catalysts modified with copper for the decomposition of ethanol.

### Nomenclature

| Symbol | Description |
|--------|-------------|
| \([\text{C}_i]\) | number of moles of C-containing \(i\) product in the outlet stream |
| \([\text{H}_2]\) | number of moles of \(\text{H}_2\) in the outlet stream |
| \([\text{H}_2\text{O}]\) | number of moles of water in the outlet stream |
| \([\text{H}_2\text{j}]\) | number of moles of \(\text{H}_2\)-containing \(j\) product in the outlet stream |
| \(R_C\) | carbon produced rate |
| \(S_{\text{H}_2}\) | selectivity for hydrogen |
| \(S_{\text{H}_2\text{O}}\) | selectivity for water |
| \(S_{\text{C}_i}\) | selectivity for C-containing \(i\) product |
| \(\nu_i\) | ratio of stoichiometric reaction coefficients |

### 2. Experimental

#### 2.1. Catalysts preparation

The Cu-Ni-Al samples were synthesised using the continuous co-precipitation method described elsewhere [6]. Briefly, an aqueous solution containing metal nitrates was mixed with another aqueous solution of \( \text{Na}_2\text{CO}_3 \). The co-precipitation process was conducted in a CSTR at constant temperature (50°C) and pH (8± 0.1). After crystallisation at 50°C for 1 h, the precipitate was filtered and washed thoroughly with distilled and deionised water. The material was dried at 80°C for 24 h in an oven. The
samples were crushed and sieved; the fraction with particle sizes between 355 and 500 μm was collected. Thermal treatment was conducted under a synthetic air flow of 50 mL·min⁻¹ at 600°C for 6 h.

2.2. Characterisation

The materials were characterised using BET surface area measurements (S_{BET}), thermogravimetry coupled with differential thermal analysis (TG/DTA), temperature-programmed reduction (H₂-TPR), X-ray diffraction (XRD) patterns, temperature-programmed oxidation (TPO/DTA), scanning electron microscopy (SEM) and Raman spectroscopy.

The H₂-TPR profiles were collected using a multipurpose system (SAMP3). A quartz tube was loaded with 100 mg of the calcined sample and placed in a temperature-controlled oven. After pretreatment at 250°C for 1 h, the temperature was increased to 880°C (10°C·min⁻¹) using 30 mL·min⁻¹ of a 10% H₂/N₂ (v/v) reduction mixture. The reduction curves were recorded with a thermal conductivity detector (TCD). The S_{BET} was also measured in the SAMP3 equipment by the N₂ dynamic adsorption method at its normal boiling point (-196°C).

Thermogravimetric analysis was performed using a TA thermobalance (Model SDT600). In these experiments, 10 mg each of fresh sample (TG/DTA) and each sample after reaction (TPO/DTA) was purged with N₂ at room temperature and then heated up to 850°C (10°C·min⁻¹) under an air flow rate of 100 mL·min⁻¹.

The powder XRD patterns were collected with a Bruker D2 Phaser X-ray diffractometer using CuKα radiation. The Ni metallic crystallite diameters of the catalysts after reaction were estimated by applying the Scherrer equation at 2θ = 44.5°. The SEM images were obtained in a JEOL JSM-6060 equipment at 20 kV under vacuum. The Raman spectra was collected using a laboratory-built micro-Raman spectrometer described earlier [8].

2.3. Catalytic evaluation

The samples were reduced in situ under an H₂ flow of 100 mL·min⁻¹ for 1 h at the same reaction temperature. The decomposition runs were carried out in a fixed bed quartz reactor (6 mm i.d.) loaded with 100 mg of catalyst diluted with quartz (1:1 v/v). The tests were performed for 90 min under atmospheric pressure at 500 and 600°C. Nitrogen and ethanol were fed at a flow rate of 100 mL·min⁻¹ and 0.5 mL·h⁻¹, respectively. The gas hourly space velocity (GHSV) was 30,000 mL·g⁻¹·h⁻¹. The products were analysed on-line by gas chromatography. The selectivity for hydrogen (S_{H2}), water (S_{H2O}) and C-containing products (S_{Ci}) was evaluated as follows:

\[
S_{H2} = \frac{[H_2]}{\sum V_j[H_2]} \quad (4)
\]
\[
S_{H2O} = \frac{[H_2O]}{\sum V_j[H_2]} \quad (5)
\]
\[
S_{Ci} = \frac{v_j[C_j]}{\sum v_j[C_j]} \quad (6)
\]
3. Results and discussion

The nominal composition, $S_{BET}$ and TG/DTA results of the samples are shown in Table 1. The surface area value of 122 m$^2$·g$^{-1}$ for the NA sample is attributed to the mixed oxides formation from hydrotalcite-type structure [9, 10]. Despite having been exposed to different temperatures during the hydrothermal treatment, the surface area found for NA is close to the values reported for Ni-Al materials prepared through the coprecipitation method [11, 12]. Table 1 also shows that the partial substitution of Ni by Cu minimally changes the surface area of the samples because the M$^{II}$/M$^{III}$ molar ratio did not change. Nevertheless, the surface area of C5NA suggests that higher amounts of copper may form aggregates that result in the loss of surface area. Additionally, the surface areas found for samples with low and intermediate copper contents (121-124 m$^2$·g$^{-1}$) are very similar to the Cu$_{0.01}$Ni$_{0.99}$O precipitate catalyst calcined at 700°C (129 m$^2$·g$^{-1}$) [13].

Table 1. Nominal composition, $S_{BET}$ and TG/DTA results of the catalyst samples

| Sample | Composition (mol %) | Ni/Cu ratio | $S_{BET}$ (m$^2$/g) | TG-DTA results |
|--------|---------------------|-------------|---------------------|----------------|
| NA     | 0 75 25             | $\infty$   | 122                 | 200 337        |
| C24NA  | 3 72 25             | 24          | 121                 | 174 366        |
| C9NA   | 7.5 67.5 25         | 9           | 124                 | 163 373        |
| C5NA   | 12.5 62.5 25        | 5           | 113                 | 149 375        |

Table 1 also shows the thermal decomposition peaks of the samples (TG/DTA). The two endothermic peaks observed for the HT materials agree with values found in the literature [6, 14, 15]. These peaks are related to the loss of interlayer water and to the dehydroxylation and decomposition of CO$_3^{2-}$ that yield mixed oxides in temperatures below 400°C [16]. It can be noted that the partial substitution of Ni by Cu shifts towards lower temperatures the first peak temperature and to higher temperatures the second peak.

Fig. 1-a shows the XRD patterns of the calcined samples, while Fig. 1-b presents the H$_2$-TPR curves. As expected for a similar Ni-Al coprecipitated material [11], the XRD patterns for the calcined samples present diffraction reflections that correspond to NiAl$_2$O$_4$ and to NiO. Moreover, the low intensity reveals a poorly crystalline structure that was also observed elsewhere for the Ni-Al samples [4, 11], which is in agreement with the high surface area values measured by $S_{BET}$ (Table 1). Fig. 1-a also shows that the crystallinity of the samples changes little with the partial substitution of nickel by copper.
The H$_2$-TPR profiles (Fig. 1-b) exhibit a reduction peak centred at 745°C for NA sample. This peak can be ascribed to the reduction of NiAl$_2$O$_4$. When Ni is partially replaced by Cu, there is a dramatic change in the TPR profile because the reduction of NiAl$_2$O$_4$ takes place at lower temperature (of approximately 200°C) compared with the NA sample. In addition, there is a peak corresponding to the reduction of CuO, which is shifted to lower temperatures as the Cu content increases (from 270°C for C24NA to 212°C for C5NA). It is noted that the size of this peak also increases. It demonstrates that only a small amount of Cu promotes the reduction of NiAl$_2$O$_4$ at lower temperatures (see C24NA sample). This observation may be related to the reduction of copper oxides at low temperatures, which provides hydrogen dissociation sites capable of reducing some metal oxides at relatively lower temperatures, as reported for precipitated Co- and Fe-based catalysts [6, 7].

The evolution of products during the decomposition of ethanol for C9NA at 500°C is shown in Fig. 2-a, while Fig. 2-b shows the TPO-DTA curves for C24NA after the decomposition of ethanol at 600°C.
It can be observed in Fig. 2-a that the selectivity towards H$_2$, CO and H$_2$O remains at the same level with time on stream, whereas the selectivity to CO$_2$ and CH$_4$ decreases. On the other hand, the C$_2$H$_4$ selectivity increases during the reaction. Therefore, the presence of C$_2$H$_4$, together with H$_2$O in the products indicates that appreciable dehydration of ethanol (eq. 2) occurred after 30 min of reaction; the decrease in selectivity to CH$_4$ and the constant selectivity to H$_2$ suggest that the decomposition of methane (eq. 3) is also favoured during the reaction. The results also indicate that other reactions that generate light gases from decomposition (eq. 1 and 7), steam reforming of ethanol with excess water (eq. 8) and water gas shift reactions (eq. 9) take place mainly at the beginning of the process.

\[
\begin{align*}
    &C_2H_5OH \rightarrow \frac{1}{2}CO_2 + \frac{3}{2}CH_4 & \Delta H_{298K} = -74 \text{ kJ mol}^{-1} \\
    &C_2H_5OH + 3H_2O \rightarrow 2CO_2 + 6H_2 & \Delta H_{298K} = 174 \text{ kJ mol}^{-1} \\
    &H_2O + CO \rightarrow CO_2 + H_2 & \Delta H_{298K} = -36 \text{ kJ mol}^{-1}
\end{align*}
\]

TPO-DTA analysis (Fig. 2-b) indicates a small weight gain between 250 and 400°C that is related to the reoxidation of metallic phase after reaction. After the reoxidation step, there is a weight loss attributed to carbon oxidation that ends at temperatures around 650°C. A greater weight loss indicates that there is higher amount of carbon on the catalyst surface. Additionally, the higher combustion temperatures of the DTA exothermic peaks related to the oxidation of carbon are related to heavier carbon.

The distribution of products obtained from the decomposition of ethanol at 500°C and 600°C after 30 min is shown in Table 2. The conversion of ethanol was 100% for all runs. Table 2 also shows the DTA peaks related to the oxidation of carbon and the carbon production rate estimated by TPO-DTA.
Comparisons between the products distributions obtained at different reaction temperatures show high selectivity towards CO\textsubscript{2} and CH\textsubscript{4} at 500°C. This result indicates that exothermic reactions such as the decomposition of ethanol to CO\textsubscript{2} and CH\textsubscript{4} (eq. 7) and the water gas shift (eq. 9) take place.

On the other hand, reactions at 600°C in general lead to higher selectivity towards H\textsubscript{2} and CO, and lower selectivity to CO\textsubscript{2}, CH\textsubscript{4} and H\textsubscript{2}O. Therefore, these results suggest that reactions that generate synthesis gas through decomposition and steam reforming of ethanol (eq. 1 and 10) and steam and dry reforming of methane (eq. 11 and 12) are favoured at higher temperatures, as expected by their stronger endothermic nature. Additionally, the results are possibly related to other reactions that produce H\textsubscript{2} and CO, such as the gasification of carbon with CO\textsubscript{2} (Boudouard, eq. 13) and water steam (eq. 14).

\[
\begin{align*}
\text{C}_2\text{H}_5\text{OH} + \text{H}_2\text{O} & \rightarrow 2\text{CO} + 4\text{H}_2 & \Delta H_{298K} = 256 \text{ kJ mol}^{-1} \\
\text{CH}_4 + \text{H}_2\text{O} & \rightarrow \text{CO} + 3\text{H}_2 & \Delta H_{298K} = 206 \text{ kJ mol}^{-1} \\
\text{CH}_4 + \text{CO}_2 & \rightarrow 2\text{CO} + 2\text{H}_2 & \Delta H_{298K} = 246 \text{ kJ mol}^{-1} \\
\text{C}(s) + \text{CO}_2 & \rightarrow 2\text{CO} & \Delta H_{298K} = 172 \text{ kJ mol}^{-1} \\
\text{C}(s) + \text{H}_2\text{O} & \rightarrow \text{CO} + \text{H}_2 & \Delta H_{298K} = 131 \text{ kJ mol}^{-1}
\end{align*}
\]

The TPO-DTA analysis summarised in Table 2 shows higher carbon formation for reactions performed at 500°C. This can be explained by the carbon consumption reactions (eq. 13 and 14), which have been assumed to take place at higher temperatures based on the products distribution (Table 2) and on their enthalpies. Nevertheless, the DTA peaks related to the combustion of carbon suggest that higher temperatures would be required for the regeneration of catalysts deactivated by carbon deposition in the decomposition of ethanol performed at 600°C.

Compared to NA, the partial substitution of Ni by Cu results in a decrease in the selectivity towards H\textsubscript{2} and CO that is observed for tests performed at 500°C and a decrease of carbon production. Moreover, it can be noted that the Cu-containing catalysts produce ethylene through the dehydration of ethanol (eq. 2), while NA does not produce these hydrocarbon compounds after 30 min of time on stream. Table 2 also shows that the dehydration reaction is enhanced when Cu content in the sample increases. These results demonstrate that Cu strongly changes the properties of the catalysts promoting the dehydration reaction (eq. 2) and decreasing the amount of CH\textsubscript{4} (eq. 1) and therefore the carbon deposition by CH\textsubscript{4} decomposition (eq. 3). Nevertheless, it can be observed that higher Cu contents lead to lower selectivities
towards synthesis gas. In addition, the DTA peaks show that the temperature required for carbon oxidation decreases with increasing Cu content.

The SEM images of the C9NA and NA catalysts after reaction at 500°C and the NA catalyst after reaction at 600°C are displayed in Fig. 3.

Fig. 3. SEM images of catalysts after reaction: (a) NA at 500°C; (b) NA at 600°C; (c) C9NA at 500°C

The images obtained for NA after reactions at 500°C and 600°C (Fig. 3-a and 3-b, respectively) appear to show carbon nanotubes with similar structures and variable diameters (between 15-40 nm). They suggest that the temperature of the reaction has little influence on the carbon nanotubes. On the other hand, the SEM image of the C9NA catalyst after reaction at 500°C suggests that the carbon nanotube structures are non-uniform in that the lengths and the diameters vary considerably. The diameter of the nanotubes in C9NA is generally larger than that of the nanotubes observed in the images for the NA catalyst. Although a decrease in Cu-loaded catalysts could not be observed due to the high reaction temperatures adopted, Fig. 3-c suggests that a copper phase was sintered during reduction and reaction. This phenomenon is supported by the H2-TPR results, which have shown that the reduction CuO → Cu0 takes place at temperatures approximately 200°C (Fig. 1-b). Moreover, this assumption is in agreement with previously reported results regarding the lower thermal stability of Cu-containing samples [17].

The XRD patterns for the NA and C9NA catalysts after reaction at 500°C and 600°C are shown in Fig. 4-a, while the Raman spectra are shown in Fig. 4-b. The XRD patterns present diffraction peaks ascribed to carbon and to metallic nickel. In addition, peaks at approximately 2θ = 35° were also observed, which is related to the small amounts of SiC that were used as a diluent and were not removed after reaction. Lindo et al. [18] observed that the intensity of the diffraction peak at approximately 26°, which was assigned to carbon, was proportional to the coke amount, as measured by TPO-DTA (Table 2). The crystallite diameters decrease in the following order: C9NA_600 (46 nm) > NA_600 (27 nm) > C9NA_500 (21 nm) > NA_600 (17 nm). Although the diameter of C9NA_500 could not be correlated to its SEM image due to the high non-uniformity of the carbon structures found for this catalyst (Fig. 3-c), the diameter of NA was close to the value estimated from the CNT diameters in Fig. 3-a and Fig. 3-b. These values indicate that higher reduction and reaction temperatures result in higher crystallite diameters, which is possibly associated with sintering. It also suggests that sintering becomes dramatically worse for samples containing copper at higher reduction and reaction temperatures (C9NA_600), resulting in diameters approximately 46 nm at the end of reaction.
The Raman spectra (shown in Fig. 4-b) exhibit two major peaks for all catalysts located at 1325-1330 cm\(^{-1}\) (D band) and 1590-1605 cm\(^{-1}\) (G band). The G band is indicative of ordered structures in the CNT, while the D band provides information regarding defects and impurities in the CNTs [19]. The ratio between the intensity of the peaks of the D band and G band (I\(_D\)/I\(_G\) ratio) indicates the perfection of the structure and purity of the CNTs. Lower I\(_D\)/I\(_G\) ratio values are associated with higher crystallinity and fewer defects on the CNT walls [3, 20]. The I\(_D\)/I\(_G\) ratio values, typically observed for multi-walled carbon nanotubes (MWCNT), decreased in the following order: C5NA_600 (1.8) < NA_500 (1.7) < C5NA_500 (1.5) < C9NA_500 (1.4) < C24NA_500 (1.3). As reported elsewhere for Ni-based catalysts [2], the results suggest that higher I\(_D\)/I\(_G\) ratio values are obtained for reactions conducted at higher temperatures. Therefore, small increases in CNTs defects and impurities are expected for reactions performed at higher temperatures. Moreover, it can be noted that the partial substitution of Ni by Cu (C24NA_500) provides nanotubes with higher purities and lower defects.

4. Conclusions

The partial substitution of Ni by copper decreases the specific surface area and shifts the reduction of NiAl\(_2\)O\(_4\) towards lower temperatures. The higher reaction temperature (600°C) results in a higher selectivity towards H\(_2\) and CO and lower carbon formation, even though the temperature required for its combustion is higher. The partial substitution of Ni by Cu decreases the selectivity for synthesis gas for runs performed at 500°C, particularly for the sample with a higher Cu content. The SEM images reveal the formation of CNTs with diameters similar to those estimated by XRD for metallic crystallites.
Additionally, the Cu-loaded sample appears to form non-uniforms CNTs with larger diameters, which is possibly associated with the sintering of copper. However, the Raman spectra suggest that CNTs with higher purities and fewer defects were synthesised by Cu-containing catalysts.

Acknowledgements

The authors thank MCT/CNPq and CAPES for their financial support.

References

[1] Gallego J, Sierra G, Mondragon F, Barrault J, Batiot-Dupeyrat C. Synthesis of MWCNTs and hydrogen from ethanol catalytic decomposition over a Ni/La$_2$O$_3$ catalyst produced by the reduction of LaNiO$_3$. Appl Catal, A Gen 2011;397:73-81.
[2] Mezalira DZ, Probst LD, Pronier S, Batonneau Y, Batiot-Dupeyrat C. Decomposition of ethanol over Ni/Al$_2$O$_3$ catalysts to produce hydrogen and carbon nanostructured materials. J Mol Catal A: Chem 2011;340:15-23.
[3] Wang G, Wang H, Tang Z, Li W, Bai J. Simultaneous production of hydrogen and multi-walled carbon nanotubes by ethanol decomposition over Ni/Al$_2$O$_3$ catalysts. Appl Catal, B 2009;88:142-151.
[4] Más V, Dieuzeide ML, Jobbágy M, Baronetti G, Amadeo N, Laborde M. Ni(II)-Al(III) layered double hydroxide as catalyst precursor for ethanol steam reforming: Activation treatments and kinetic studies. Cat Today 2008;133:319-323.
[5] Resini C, Montanari T, Barattini L, Ramis G, Busca G, Presto S et al. Hydrogen production by ethanol steam reforming over Ni catalysts derived from hydroxalcite-like precursors: Catalyst characterization, catalytic activity and reaction path. Appl Catal, A Gen 2009;355:83-93.
[6] Hermes NA, Lansarin MA, Perez-Lopez OW. Catalytic Decomposition of Methane Over M-Co-Al Catalysts (M = Mg, Ni, Zn, Cu). Catal Lett 2011;141:1018-1025.
[7] Wan H, Wu B, Zhang C, Xiang H, Li Y. Promotional effects of Cu and K on precipitated iron-based catalysts for Fischer-Tropsch synthesis. J Mol Catal A: Chem 2008;283:33-42.
[8] Balzaretti NM, Gallas MR, Costa TMH, Stefani V, Perrottoni CA, da Jornada JAH. Raman investigation of 2,5-bis(benzoxazol-2'-yl)4-methoxyphenol under high pressure. J Raman Spectrosc 2003;34:244-247.
[9] Vaccari A. Clays and catalysis: a promising future. Appl Clay Sci 1999;14:161-198.
[10] Trifirò F, Vaccari A. Hydrotalcite-like anionic clays (layer double hydroxides). In: Atwood JL, Davies JED, editors. Comprehensive Supramolecular Chemistry, Oxford: Pergamon; 1996, p. 251-291.
[11] Martinez R, Romero E, Guimon C, Bilbao R. CO$_2$ reforming of methane over coprecipitated Ni-Al catalysts modified with lanthanum. Appl Catal, A Gen 2004;274:139-149.
[12] Kovanda F, Rojka T, Bezdicka P, Jiratova K, Obalova L, Pacultzova K et al. Effect of hydrothermal treatment on properties of Ni-Al layered double hydroxides and related mixed oxides. J Solid State Chem 2009;182:27-36.
[13] Wang F, Li Y, Cai W, Zhan E, Mu X, Shen W. Ethanol steam reforming over Ni and Ni-Cu catalysts. Catal Today 2009;146:31-36.
[14] Vaccari A. Preparation and catalytic properties of cationic and anionic clays. Catal Today 1998;41:53-71.
[15] Palmer SJ, Spratt HJ, Frost RL. Thermal decomposition of hydrotalcites with variable cationic ratios. J Therm Anal Calorim 2009;95:123-129.
[16] Lopez-Salinas E, Garcia-Sanchez M, Luisa Ramon-Garcia M, Schiffer I. New Gallium-Substituted Hydrotalcites: [Mg$_{x}$Ga$_{y}$((OH)$_{2}$)$_{z}$]CO$_3$.mH$_2$O. J Porous Mater 1996;3:169-174.
[17] Souza G, Perez Lopez OW. Desenvolvimento de catalisadores Fe-Al modificados e sua aplicação no processo GTL visando a obtenção de combustíveis líquidos. In: XXII CICAT - Congreso Iberoamericano de Catálisis, Viña del Mar: FISIOCAT; 2010, p. CE-P-152.
[18] Lindo M, Vizcaíno AJ, Calles JA, Carrero A. Ethanol steam reforming on Ni/Al-SBA-15 catalysts: Effect of the aluminium content. *Int J Hydrogen Energy* 2010;35:5895-5901.

[19] Li WZ, Zhang H, Wang CY, Zhang Y, Xu LW, Zhu K, Xie SS. Raman characterization of aligned carbon nanotubes produced by thermal decomposition of hydrocarbon vapor. *Appl Phys Lett* 1997;70:2684-2686.

[20] Nakamura K, Fujitsuka M, Kitajima M. Disorder-induced line broadening in 1st-order Raman-scattering from graphite. *Phys. Rev. B: Condens Matter Mater Phys* 1990;41:12260-12263.