



“Steam reforming of ethanol for hydrogen production using Ni-W/CeO₂, Ni-W/ γ -Al₂O₃ and Ni-W/HT catalysts”

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ABSTRACT

Ni-W catalysts supported on CeO₂, Al₂O₃ and Hydrotalcite (HT) were studied in the steam reforming of ethanol at 500-650°C. The CeO₂ and HT were synthesized by impregnation and direct coprecipitation methods, respectively. Commercial Al₂O₃ was used. Nickel content was varied from 10, 15 and 30% with 1% W. 10% Ni-W/HT was the catalyst that presented the highest catalytic activity and selectivity to hydrogen. Conversion to ethanol was 100% and selectivities to H₂, CH₄, CO₂ and CO were 75, 5.78, 0.37 and 18.85% respectively, at a temperature of 500°C. Moreover, these catalysts showed good stability with respect to carbon deposition and low selectivity towards C₂H₄ production. These are desirable features for catalysts to be used in hydrogen production for fuel cell applications.

Key words: Hydrotalcite, steam reforming, ethanol, hydrogen.



1. INTRODUCTION

The interest in hydrogen as an alternative energy has increased due to the environmental aspects. Although there are transportation and storage problems of hydrogen, on board reforming of hydrocarbons especially alcohols makes this energy option attractive. Among alcohols, ethanol is low in toxicity, easy to store and transport, renewable and gives hydrogen rich mixture when it decomposes. For this reason many researchers studied steam reforming of ethanol with many different kinds of materials [1], [2], [3].

In this study, Ni-W/CeO₂, Ni-W/ γ -Al₂O₃ and Ni-W/HT catalysts were synthesized, characterized and used for the steam reforming of ethanol to produce hydrogen. The effects of reaction temperature, space time, metal/Ni ratio in the catalysts and the synthesis method were observed. When metal integrated onto this material, it shows higher activities to a number of reactions. Ni is one popular metal used incorporated on catalysts used for steam reforming. The complete conversion of ethanol high hydrogen selectivity and yield are important factors affecting the process economy. At this point, catalyst plays significant role in resulting reactions since each catalyst induces different reaction paths. So the selection of the suitable catalyst is really crucial [4], [5].

2. EXPERIMENTAL.

2.1 Preparation of Ni-W / CeO₂ catalysts. The synthesis method of Ni-W catalysts supported on CeO₂ was incipient wetness impregnation using an aqueous solution of ammonium metatungstate (NH₄)₆W₁₂O₃₉ • H₂O (Aldrich) on CeO₂ support, which was prepared, then nickel nitrate solution Ni (NO₃)₂ • 6H₂O (JT Baker) was added, yielding a homogeneous precursor, which was dried at 75 °C overnight and then calcined at 500 °C by 4hrs. Preparation of cerium oxide support consisted in hexadecylamine (C₁₆H₃₅N) (Aldrich) as surfactant and cerium acetate (Aldrich) as precursor of CeO₂ (Ce (CH₃COO)₃, 1.5 H₂O).

2.2 Preparation of catalysts Ni-W / γ -Al₂O₃. The synthesis method of supported Ni-W catalysts was incipient wetness impregnation using an aqueous solution of ammonium metatungstate (NH₄)₆W₁₂O₃₉ • H₂O (Aldrich) on γ -Al₂O₃ support (commercial *Keftel*), then

the nickel nitrate solution $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ was added. A homogeneous precursor was obtained, which was dried at 75°C overnight and then calcined at 550°C for 3hrs.

2.3 Preparation of catalysts Ni-W/HT. The synthesis of hydrotalcite solid basic catalysts was performed by the direct coprecipitation method [6-7]. The prepared solids were called Ni-W/Mg-Al series. These series were obtained from the procurement of hydrotalcite support from precursor $\text{Mg}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (Aldrich) and $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (Aldrich) salts and precipitating NaOH (JT Baker) and Na_2CO_3 (JT Baker) agents, so a third $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (JT Baker) solution was added. Once obtained this suspension, a fourth solution of $(\text{NH}_4)_6\text{W}_{12}\text{O}_{39} \cdot \text{H}_2\text{O}$ (Aldrich) was also added. The theoretical molar Mg/Al ratio was 2.1. In all cases, solids were synthesized at different metal concentrations (10, 15 and 30% Ni and 1% W), the pH was controlled from 10 to baseline conditions of agitation and constant temperature of 30°C , and so they could be entered or processed to heating treatment at 120°C for 10h.

2.4 Characterization of the catalysts.

The X-ray diffractograms were recorded before and after the chemical reaction in a Rigaku DMAX 2200 equipment operated and equipped with an emitter of radiation $\text{CuK}\alpha$ ($\lambda = 0.15418\text{ nm}$) at a rate of $2\theta = 20^\circ\text{C}$ and 100°C was used.

The decomposition of the catalyst was studied by thermogravimetry in a Shimadzu TGA51 under a N_2 flow (50ml/min), from room temperature to 1000°C with a heating rate of $10^\circ\text{C min}^{-1}$.

Analysis by scanning electron microscopy (SEM) and elemental analysis (EDS) of samples before and after the catalytic evaluation were obtained in a Jeol JSM - 5335C.

The specific surface area was determined by N_2 adsorption at -196°C by the BET method using a Micromeritics Accusorb 2100E.

3. CATALYTIC TESTS.

The activation of the catalysis was performed by increasing the temperature at 550°C in a hydrogen-flux during 60 min. In order to active the catalyst, the temperature was raised from ambient temperature to 550°C , in a flow of hydrogen during 60 min. Then, it was cooled

down to 300°C, also in hydrogen flux, during 60 min. The experimental equipment for the studies of ethanol steam reforming. 1g of catalyst was loading in the U-shaped stainless steel reactor (7mm internal diameter). The reactions were tested under differential reactor conditions. The feed of reactants (water steam and ethanol) to the reactor was supplied with a micrometric needle valve. A constant mixture of N₂ and H₂O/CH₃CHOH with a molar ratio of 4/1 was supplied in gas flow with two steel saturator and this mixture was vaporized and maintained at 85°C, before entering the reaction chamber.

The analysis of the reactants and reaction products was carried out by gas chromatography (Varian and Gow-Mac equipment). The samples were divided in two aliquots by an automated injection valve; one of them was used for analized H₂, CO, CO₂ and CH₄, using silica gel column packet of 12 grade (60/80) with a Thermal Conductivity Detector (TCD). The second aliquot was used to analyze the species: CH₃CH₂OH, CH₃CHO, and C₂H₄ with a capillary column (VF-1ms, 15m x 0.25 mm x 0.25 µm) in a Varian chromatograph CP-3380 with a flame ionization detector (FID).

Response factors for all products were obtained and the system was calibrated with appropriate standards before each catalytic test. The conversion (X) was calculated using the ethanol composition before and after the reaction. The selectivity was defined as the mole fraction of each product as follows:

$$S_x = \frac{n_x}{\sum n_i} \quad (1)$$

Where S_x is the selectivity of x, n_x is the mole of product x, n_i is the mole for each product (included x). The water was not included.

4. RESULTS AND DISCUSSION

In Figure 1 presents diagrams of X-ray diffraction of samples, both before / after reaction (A/R and B/R). The diffraction pattern of the FC-1 catalyst is shown in Figure 1 (a). XDR patterns of pure CeO₂ show that the main diffraction planes are (111), (200) (220), (311) and (422). See Figure 1(a). The crystal structure for this cerium oxide is fluorite [8]. In conducting the impregnation with 10% of Ni and 1% of W, it appears that the new formed

compound has the following features of diffraction; there is no significant change in the diffraction spectra, as shown in Figure 1(b). However, when it is subjected to the ethanol-reforming process, it is observed that the intensity of the diffraction of CeO_2 increases and the diffraction peaks appears. In the case of impregnated samples were two phases of the medium (CeO_2) and nickel oxide (NiO). The diagrams of the reaction in Figure 1 showed more intense Ni metal peaks and the ones of NiO disappeared. These diagrams showed that during the catalytic process the reduction of nickel oxide to nickel metal was performed, which may indicate that the medium facilitated the reduction of nickel. This caused that the present NiO in the samples was reduced more easily under conditions in which catalytic tests were carried out.

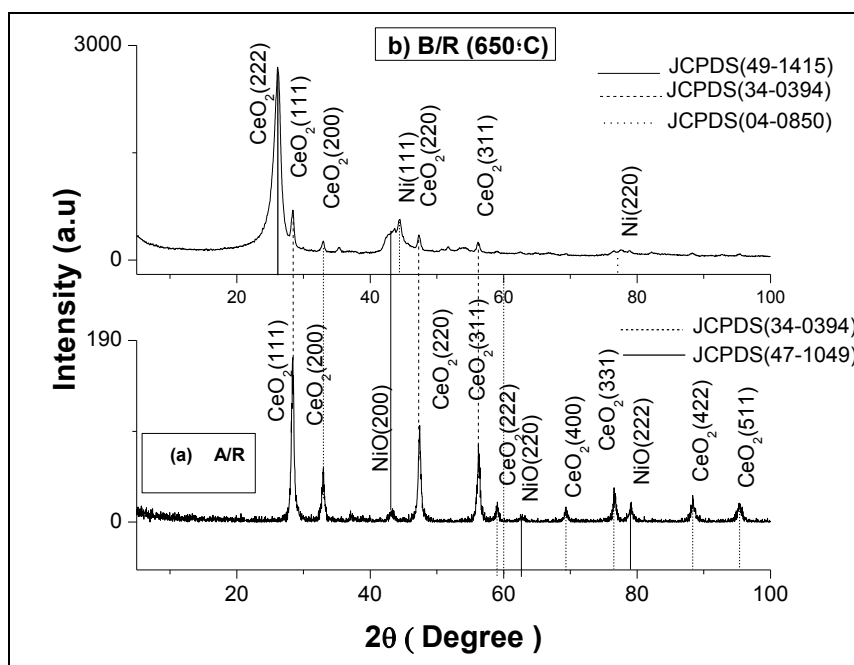


Figure 1. XRD Diffraction patterns of the Ni-W/ CeO_2 catalysts.

4.1 Scanning electron microscopy (SEM) of the Ni-W/ CeO_2 (CF-1) catalyst.

The scanning electron microscopy was used to observe the catalysts morphology before and after the reaction. Figures 2(a) and (b) compare the morphology of the obtained particles in each case (A/R and B/R), respectively. The first consists of relatively regular crystal

agglomerates of about 10 micrometers. However, once exposed to the reforming reaction is observed that the agglomerate size decreases, from 1 to 5 micrometers.

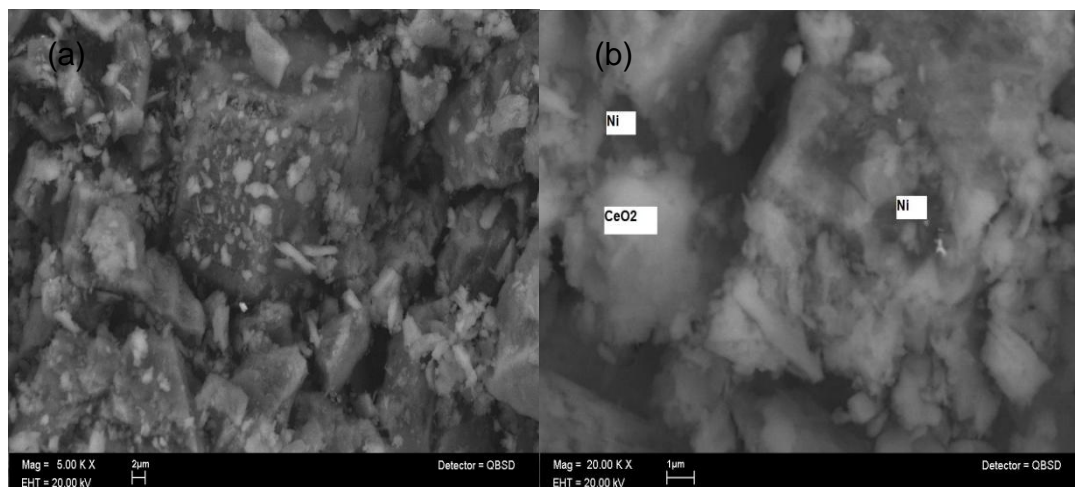


Figure 2. Scanning electron microscopy (SEM) images for the Ni-W/ Al_2O_3 catalyst: before (a) and after the reaction (b).

4.2 X-ray diffraction of the Ni-W/ Al_2O_3 (AF1) catalyst.

The diffraction patterns of the catalysts based on Ni supported on Al_2O_3 and W before and after the reaction are presented in Figure 3 (a) and (b), respectively.

The diffraction patterns of the samples used in the reaction presented in Figure 4 show the characteristic peaks for the phases of Al_2O_3 (220), (311), (400), (511) y (440) JCPDS(10-0425). The peaks of NiO (200), (220) y (311) JCPDS(47-1049), as it is shown in Figure 4 (a). By submitting this catalyst to a temperature range between 400 and 650 °C, a spectrum of X-ray showing the peaks of Al_2O_3 (311) y (440), Ni (111), (200) y (220), and the peaks of NiAl_2O_4 (422) JCPDS(10-0339). The formation of NiAl_2O_4 phase is obtained when the catalyst was subjected to the reforming reaction, which becomes evident since the active phase is interacting with the media.

4.2.1 Scanning electron microscopy (SEM) of the Ni-W/ Al_2O_3 (AF1) catalyst.

The images show agglomerated particles with an irregular morphology and heterogeneity in size. The particle size varies according to the content of Ni, for the AF-1 sample an approximate size covers from 10 to 100 micrometers. See Figure 4 (a), A/R which corresponds to the catalyst without subjecting it to the reaction. For this sample after (B/R)

reaction, there are structures of carbon nanotubes which are not evident in the Ni-W/CeO₂ catalyst. Figure 4 (b) B/ R.

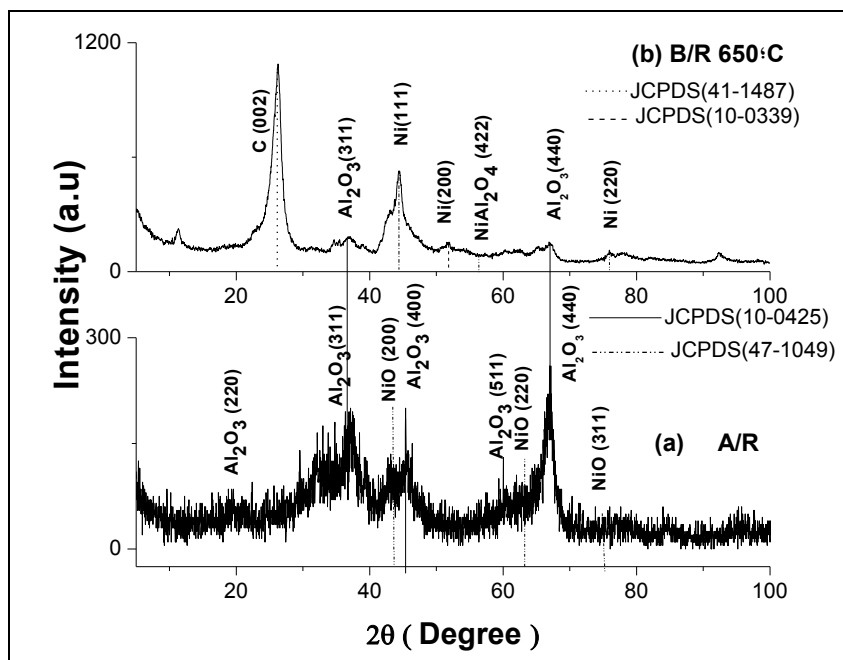


Figure 3. Diffraction patterns of the XRD analysis of the of the Ni-W/Al₂O₃ catalysts.

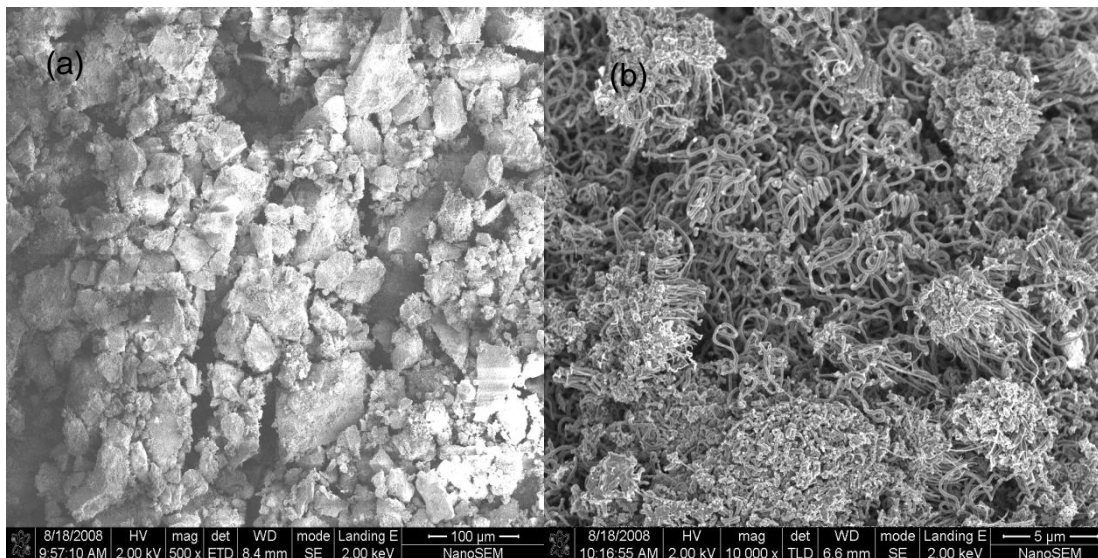


Figure 4. Scanning electron microscopy (SEM) images for the Ni-W/Al₂O₃ catalyst: (a) before and (b) after the reaction.

4.3 X-ray diffraction of the Ni-W/HT (HF1) catalyst.

The diffractograms on Figure 5 (a) show the characteristic peaks of the hydrotalcite-type compound with the indices of (003), (006), (101), (015), (018), (0110) y (113) for hydrotalcite JCPDS (35-0964). In subsection (b) the peaks after the reaction of Ni (010), (011) y (103) JCPDS (45-1027), the peaks of MgAl_2O_4 (220) and (404) with JCPDS (21-1152) and the peaks of HT (004), (113) and (116) JCPDS (35-0964), are shown. The calcined hydrotalcite has the ability to reconstruct the initial lamellar structure when contacted with aqueous solutions containing the initial anion or another; a process called memory effect typical of hydrotalcites.

4.3.1 Scanning electron microscopy (SEM) for the Ni-W/HT (HF1) catalyst.

For samples of the Ni-W/HT series, SEM images show particles with irregular morphology and heterogeneity in size between 50 to 300 micrometers approximately, Figure 6. The particles show facets on some faces with smooth surface and others with porosity constituted of layers with a distance among them of approximately 2.8 μm layers with a laminar structure. BET analysis of the Ni-W/ CeO_2 (CF-1), Ni-W / $\gamma\text{-Al}_2\text{O}_3$ (AF-1) and Ni-W/HT (HF-1) catalyst. The results show that the effect of the reaction on BET areas for CF-1 decreases from 23.65 and 22.56 m^2/g to 11.85 and 17.54 m^2/g respectively, when increasing the reaction temperature of 300 ° C to 650 ° C. This decrease in area is attributed to sintering, which leads to particles agglomeration. As decreasing the size of glass, the area decreases and the pore diameter increases.

For the AF-1 sample, it was observed that after the reaction the BET area decreases from 94.43 and 81.71 m^2/g to 82.45 and 76.45 m^2/g respectively, as temperature increases. In this case the decrease in area has been attributed to sintering, which leads to particles agglomeration. As increasing the size of crystal the area decreases and the pore diameter increases.

In the HF-1 samples after the reaction the BET area increases from 185.38 (A/R) and 135.59 m^2/g (B/R) to 216.57 and 165.59 m^2/g respectively as temperature increases. The increase of

area was attributed neither to sintering in these catalysts nor particles agglomeration. As decreasing the size of glass, the area increases and the pore diameter decreases.

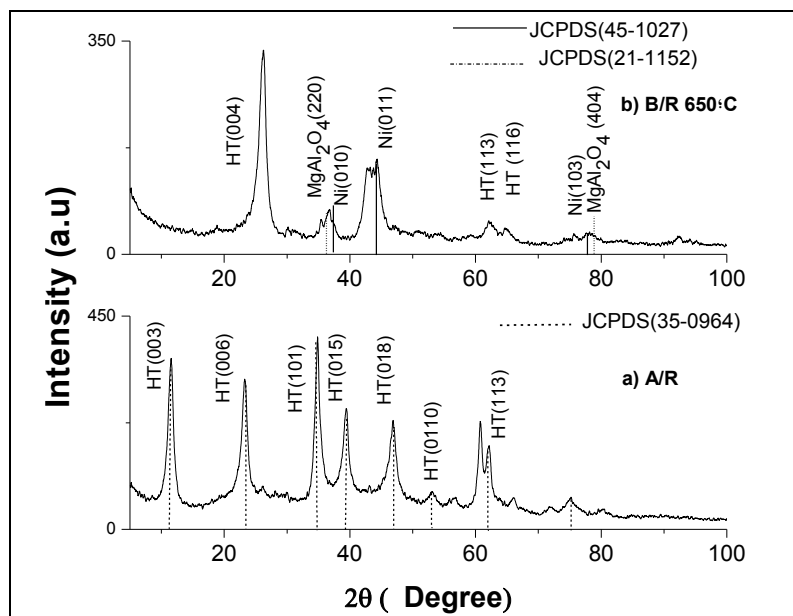


Figure 5. Diffraction patterns of the XRD analysis of the 10%Ni-W/HT catalysts.

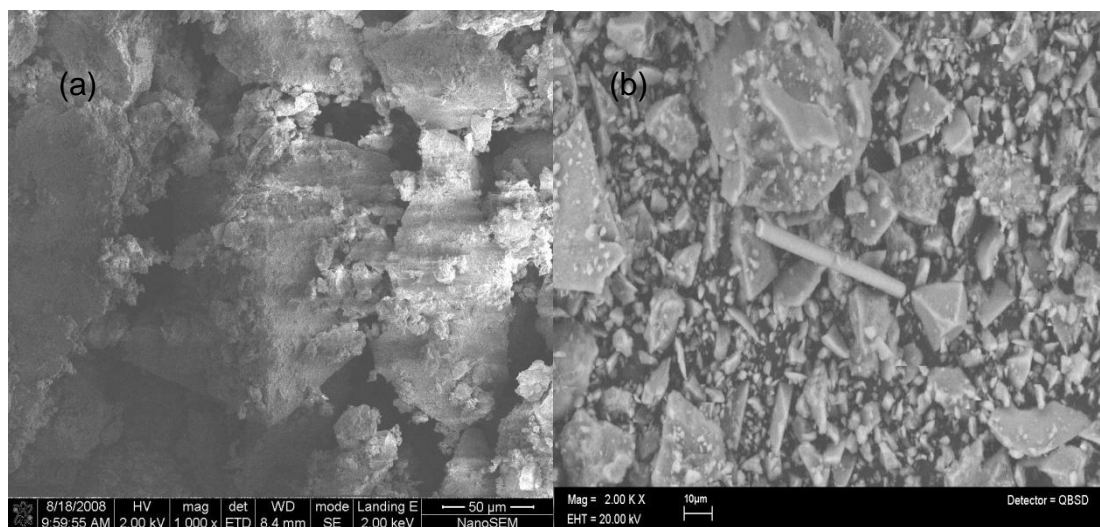


Figure 6. Scanning electron microscopy (SEM) images for the 10%Ni-W/HT catalyst: before (a) and after the reaction (b).

5. CATALYTIC EVALUATION

Measurements at variable and constant temperature contact time. The series of catalysts called CF, AF and HF (Ni-W/CeO₂, Ni-W/Al₂O₃ and Ni-W/HT) respectively, were tested for the reforming reaction of ethanol from a contact time $W / F = 1.65 \text{ g.hr / mol}$ and various reaction temperatures: 300-650 °C. Ethanol conversion and selectivity results for H₂ at different temperatures and reaction products. In Figure 7 is represented by the H₂ selectivity depending on reaction temperature. It is noted that both the total conversion and H₂ selectivity increased with temperature for all catalysts.

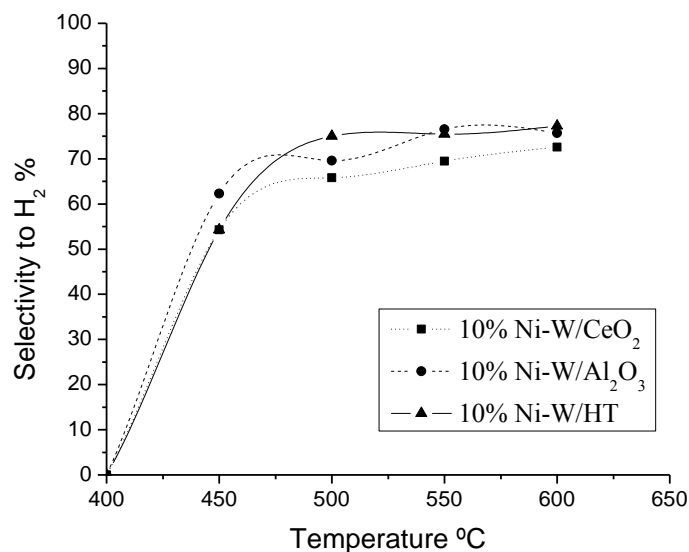


Figure 7. Temperature effect on the H₂ selectivity for the catalysts. Water/Ethanol molar ratio is: 4 / 1.

6. COMPARISON OF THE CATALYTIC EVALUATION, THE THREE CATALYTIC SYSTEMS.

We performed a comparison of the series of catalysts at a temperature of 500 °C and 10% Ni-W of the active phase to be varied, called CF-1, AF-1 and HF-1. The catalysts were also active, with conversions of 100% ethanol. At this temperature, other products are obtained. Shown in Figure 8, for all cases no acetaldehyde is formed, for CF-1 and AF-1 is formed ethylene (C₂H₄) and in all cases the selectivity to CO is very low, from less than 1-3%, noting

that the amount for HT-1 is almost zero, similar to that reported in other catalytic systems. [9],[10], [11]. It also has a higher selectivity for H₂, HT-1, AF-1 and CF-1 respectively.

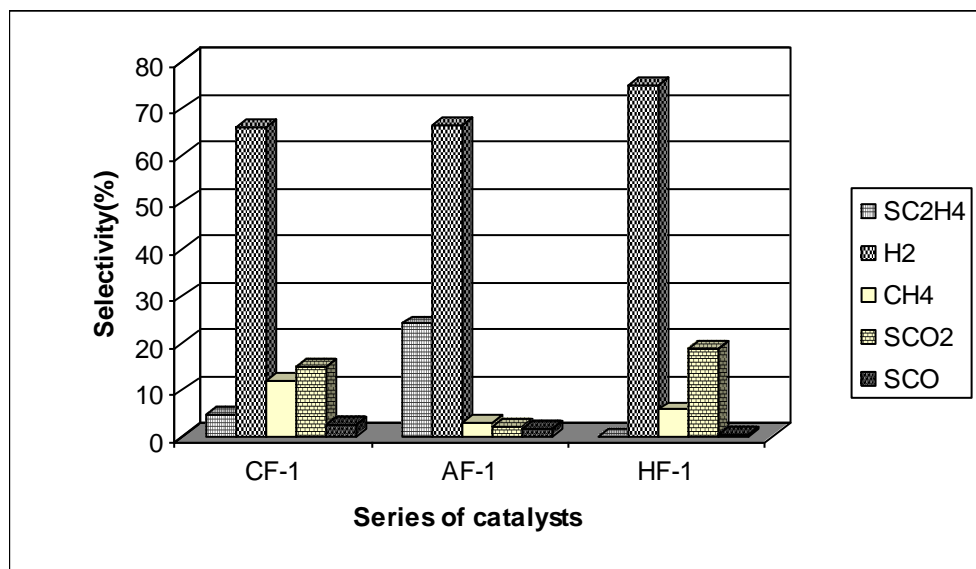


Figure 8. Comparison between the different catalytic systems

7. DEACTIVATION.

Different types of catalysts showed to be stable at 6 h, it was proposed to work 21h with the series: CF-1, AF-1 and HF1 for different stages of deactivation. In Figure 9 shows the deactivation of the catalysts. Nothing where the graph we can say that in this period of time for Ni-W/HT catalyst deactivation is not observed, because the conversion remains constant during the reaction time. For the catalyst Ni-W/CeO₂ there is a 6h drop reaction, one drop at 15 h and finally remains constant at 21 h of reaction with a final conversion of 98.9%. It also showed that the catalyst deactivation was the most significant catalyst Ni-W/Al₂O₃, which starts 12hrs from their conversion to fall until stabilized at 21 h with a conversion of 87.7%.

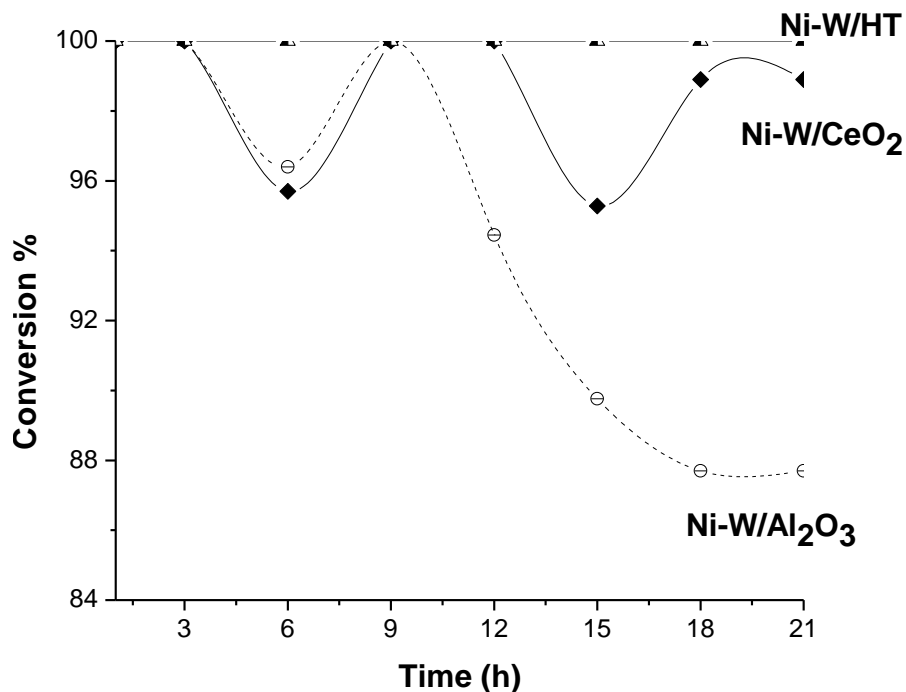


Figure 9. Deactivation of the Ni-W / supported catalysts of the series a 20h reaction continues in Steam Reforming.

8. CONCLUSIONS

Catalysts have been prepared Ni-W/CeO₂, Ni-W/Al₂O₃ and Ni-W/Ht with loads of metallic Ni from 10-30% by the method of incipient precipitation for the first two and the third co-precipitation catalyst.

The precipitation method has proven to be an interesting alternative for the preparation of solid catalysts in a wide range of loads, resulting in particle medium size, with a remarkable uniformity in size and dispersion on the support.

Likewise coprecipitation method proved to be a very interesting alternative for the preparation of hydrotalcites, leading to a large surface area and average particle sizes, with a considerable uniformity in their size and dispersion of the medium. This method has the main features of its simplicity, control of stoichiometry and economic viability for a possible industrial scale.

The catalysts prepared for Ni-W/CeO₂ showed two well-defined phases before the reaction: NiO and CeO₂, after the reaction metallic nickel and alumina. The catalysts showed a reduction in surface area, after the reforming reaction, a specific surface which can be considered notable for the type of material and the reaction temperature of 500-650°C. For catalysts Ni-W/Al₂O₃, have also two well-defined phases, before the reaction: NiO and Al₂O₃, and after the reaction is formed nickel metal and alumina. These catalysts also showed a reduction in surface area after the reforming reaction.

Finally, Ni-W/HT catalysts presented the stage of hydrotalcite and the Ni-W/HT and added after the reaction of MgAl₂O₄.

All the catalysts were evaluated for the reaction of steam reforming of Ethanol using a ratio of 4 / 1.

Nothing that the catalysts showed no carbon nanofibers are incurred hydrotalcites addition to these catalysts were reactivated and continued to maintain their activity without deactivation at any time.

9. REFERENCES

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