

Comparative Study of Ni-W/CeO₂, Ni-W/ γ -Al₂O₃ and Ni-W/HT Catalysts for H₂ Production by Steam Reforming of Bioethanol

Paz Hernández¹, Arturo Fernández² and Sarah Messina¹

¹Universidad Autónoma de Nayarit Ciudad de la Cultura "Amado Nervo" Tepic, Nayarit. C.P. 63155 México.

²Centro de Investigación en Energía de la UNAM Privada Xochicalco S/N Temixco, Morelos, México.

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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. The catalyst that presented the highest catalytic activity and selectivity to hydrogen was 10% Ni-W/HT. 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.

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 has low toxicity, is 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 [1-3].

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 details

2.1 Preparation of Ni-W/CeO₂ catalyst.

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 a 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 4 h. Preparation of cerium oxide support consisted in hexadecylamine (C₁₆H₃₅N) (Aldrich) as surfactant and cerium acetate (Aldrich) as precursor of CeO₂ (Ce(CH₃COO)₃·1.5H₂O).

2.2 Preparation of Ni-W/ γ -Al₂O₃ catalyst.

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 (comercial), then the nickel nitrate solution Ni(NO₃)₂·6H₂O was added. A homogeneous precursor was obtained, which was dried at 75 °C overnight and then

calcined at 550 °C for 3 h.

2.3 Preparation of Ni-W/HT catalyst.

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 Mg(NO₃)₂·6H₂O (Aldrich) and Al(NO₃)₃·9H₂O (Aldrich) salts and precipitating NaOH (JT Baker) and Na₂CO₃ (JT Baker) agents. After this, a third Ni(NO₃)₂·6H₂O (JT Baker) solution was added. Once this suspension was obtained, a fourth solution of (NH₄)₆W₁₂O₃₉·H₂O (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 10 h.

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 CuK α (λ = 0.15418 nm) at a rate of 2 θ = 20 °C and 100 °C was used.

The decomposition of the catalyst was studied by thermogravimetry in a Shimadzu TGA51 under a N₂ flow (50 mL/min), from room temperature to 1000 °C with a heating rate of 10 °C min⁻¹.

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

The specific surface area was determined by N₂ adsorption at -196 °C by the BET method using a Micromeritics Accusorb 2100E.

2.5 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. For the studies of ethanol steam reforming, 1 g of catalyst was loading in the U-shaped stainless steel reactor (7 mm 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 saturators 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 analyzed 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 μ m) 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:

$$S_x = \frac{n_x}{\sum n_i}$$

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.

3. Results and discussion

3.1 Catalytic evaluation.

The measurements were carried out 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 g-h/mol and various reaction temperatures: 300 - 650 °C. Ethanol conversion and selectivity results for H₂ at different temperatures and reaction products. Figure 1 shows the H₂ selectivity at different reaction temperatures. It is noted that both the total conversion and H₂ selectivity increased with temperature for all the catalysts.

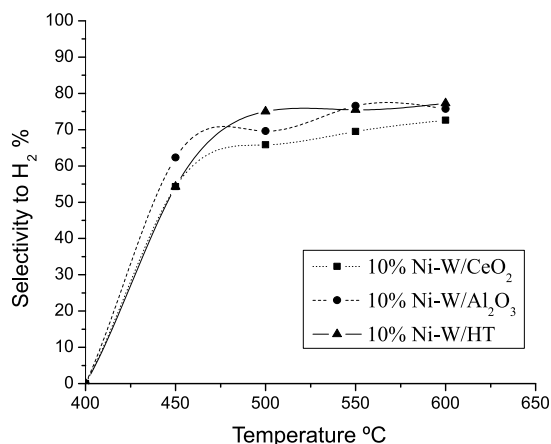


Figure 1. H₂ selectivity at different temperatures for all the catalysts. Water/bioethanol molar ratio is: 4:1.

3.2 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 2, 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, less than 1-3%, noting that the amount for HT-1 is almost zero, similar to that reported in other catalytic systems [9, 10]. It also has a higher selectivity for H₂, HT-1, AF-1 and CF-1.

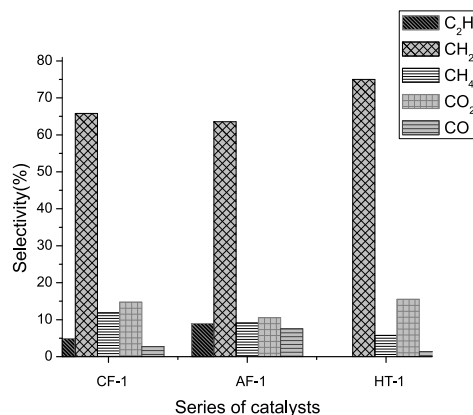


Figure 2. Comparison between the different catalytic systems

3.3 Deactivation.

Different types of catalysts showed to be stable at 6 h, it was proposed to work for 21 h with the series: CF-1, AF-1 and HF1 to watch the different stages of deactivation. In figure 3 the deactivation of the catalysts is shown. 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 6 h 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 for the catalyst Ni-W/Al₂O₃, which starts 12 h from their conversion to fall until stabilized at 21 h with a conversion of 87.7%.

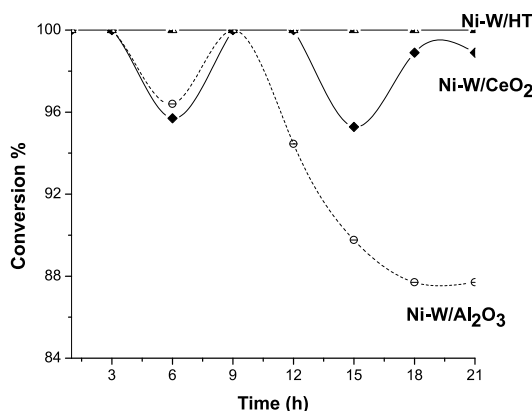


Figure 3. Deactivation of the Ni-W / supported catalysts of the series a 20 h reaction continues in steam reforming.

4. Conclusions

The catalysts Ni-W/CeO₂, Ni-W/Al₂O₃ and Ni-W/HT have been prepared with loads of metallic Ni from 10 - 30% by the method of incipient precipitation for the first two catalysts and by co-precipitation for the third 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 advantages 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 that 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.

Noting 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.

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