Ethylene glycol-modified CeO$_2$-SiO$_2$ support for Ni catalysts applied in the ethanol steam reforming (O-19H)

M. Jaramillo-Baquero[1*], J. F. Munera[1], L. M. Cornaglia[1**]

[1] *Instituto de investigaciones en Catálisis y Petroquímica- INCAPE (UNL-CONICET), Santiago del Estero 2829, S3000, Santa Fe, Santa Fe, Argentina*

(*) Pres. author: jaramillob.marcela@gmail.com   (**) Corresp. author: lmcornag@fiq.unl.edu.ar

1. Introduction

In order to mitigate the environmental impact generated by the use of fossil fuels such as oil, coke and natural gas, the possibility of generating hydrogen from renewable sources has been proposed as an alternative in recent years. Among the most attractive processes, ethanol steam reforming plays a key role due to the multiple advantages, such as low cost, easy of transportation and the possibility of producing hydrogen in relatively mild conditions, with high efficiency [1].

However, the ethanol steam reforming (ESR) reaction has a complex reaction pathways and different by-products such as carbon monoxide, methane, ethylene, acetaldehyde and carbonaceous species, can be generated. Hence, it is necessary to develop catalysts that are active, stable and selective under moderate temperature conditions (450-600 °C).

The most studied materials for this reaction are catalysts based on noble metals, which exhibit excellent catalytic properties [2,3]; however, their high cost represents a disadvantage for their use on a larger scale. Therefore, catalysts based on Ni, Co and Cu are considered an interesting alternative as active phase in the ethanol steam reforming reaction since they have high catalytic activity and low cost compared to other metals [4].

Nevertheless, the main cause of deactivation is related to carbon deposition. In order to improve the catalytic properties, it has been suggested the use of supports that provide a higher interaction with the active phase, a high specific surface that favors dispersion, and promote the oxidation of carbonaceous deposits. In addition, it has been reported that the use of binary systems can improve the properties of CeO$_2$ as a support [5].

Furthermore, in order to increase the dispersion and reducibility of Ni particles and favor hydrogen production, it has been reported that increasing the concentration of Si-OH sites by treating silica with ethylene glycol leads to the formation of smaller supported metal particles [6]. Thus, in this work, ethylene glycol-modified Ni/CeO$_2$-SiO$_2$ catalysts were synthesized and compared with the unfunctionalized material in the ethanol steam reforming reaction for hydrogen production.

2. Experimental

2.1 Synthesis of supports and catalysts

The synthesis of support and catalysts was carried out by incipient wetness impregnation. The silica source used was high surface silica (Aerosil 200 m^{2}g^{-1}). Nickel acetate C$_4$H$_6$O$_4$Ni·4H$_2$O (98%, Sigma Aldrich) and cerium nitrate Ce(NO$_3$)$_3$·6H$_2$O (99%, Sigma Aldrich) were used as precursor salts.

In the case of the functionalized material, the silica was previously pretreated with ethylene glycol (EG) by incipient wetness impregnation. Subsequently, the sample was dried in air at 393 K for 12 h. Then, 10 wt.% CeO$_2$ was added and finally the active phase was impregnated with Ni (5 wt.%). After each impregnation, the materials were dried in air at 353 K for 12 h and then calcined at 823 K for 6 h.

2.2 Catalytic evaluation

Catalytic evaluation of the catalysts in the reforming reaction was carried out in a quartz tubular reactor. 20 mg of catalyst (W/F=4.9x10^{-3} g h L^{-1}) diluted in 60 mg of quartz was loaded. The catalytic bed was heated in Ar flow until the reaction temperature (500 °C) was reached, then the catalysts were subjected to a reduction treatment in H$_2$ flow for 2 h. The reaction mixture diluted in Ar, water/ethanol (0.5 mL·min^{-1}) with a molar ratio of 5, was fed to an evaporator operating at 220 °C. All products and reagents were analyzed by gas chromatography.

2.3 Catalyst characterization

The crystalline structure of the calcined solids was characterized using a PANalytican Empyrean equipment with Cu Kα radiation, working with a voltage of 30 Kv and 40mA. The scanning speed was 2°·min^{-1} for 2θ angles between 10° and 80°.

Raman spectroscopy was employed to characterize the catalysts calcined and used in reaction, using a LabRam spectrometer (Horiba-Jobin-Yvon) coupled to an Olympus microscope (50X), equipped with a CCD detector. The excitation source was 532 nm from a Spectra Physics solid state laser.

In addition, other techniques such as X-ray photoelectron spectroscopy (XPS) and transmission electron microscopy (TEM) were employed.

3. Results

3.1 Catalytic activity

Figure 1 compares the conversion of the ethylene glycol modified and unmodified catalyst. A marked difference can be observed, resulting in the $Ni/CeO_2-SiO_2(EG)$ being more active during the 7 hours of reaction.
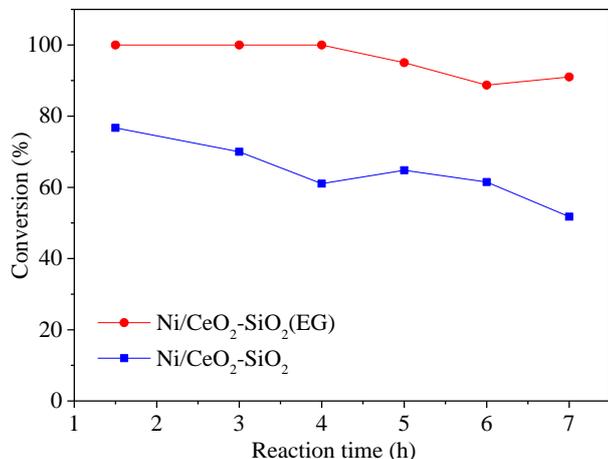

Fig 1. Ethanol conversión for Ni/CeO_2-SiO_2 and $Ni/CeO_2-SiO_2(EG)$ to W/F= $4.9x10^{-3}$ g h L^{-1}. T=500 °C. P= 1atm. R=5.

Figure 2 shows the hydrogen yield of the catalysts with and without functionalization in the reforming reaction, where it is evident that by pretreatment of the silica with ethylene glycol it is possible to double the hydrogen yield.
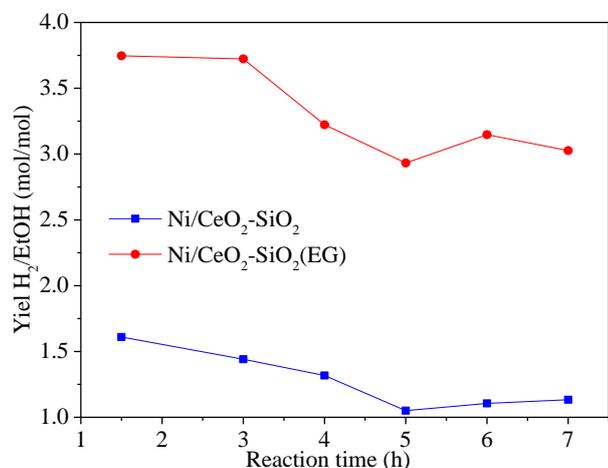

Fig. 2. Hydrogen performance for $Ni/CeO_2-SiO_2(EG)$ and Ni/CeO_2-SiO_2 . W/F= $4.9x10^{-3}$ g h L^{-1}. T=500 °C. P= 1atm. R=5.

Subsequently, in the product distribution presented in Figure 3, it is observed that using the unfunctionalized catalyst, about 10% of acetaldehyde is obtained in the reaction stream. On the contrary, for the functionalized catalyst, it was possible to obtain an acetaldehyde-free stream during the first 4 hours of reaction and after 7 h of reaction, the acetaldehyde produced was less than 1%.
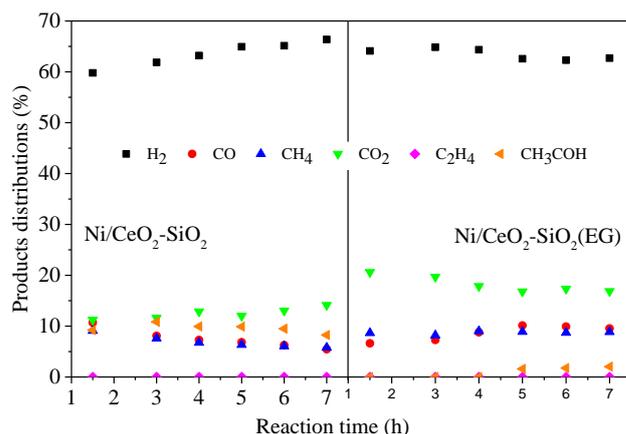

Fig. 3. Distribution of products for Ni/CeO_2-SiO_2 and $Ni/CeO_2-SiO_2(EG)$. W/F= $4.9x10^{-3}$ g h L^{-1}. T=500 °C. P= 1atm. R=5.

3.2 Catalyst characterization

Figure 4 shows the Raman spectra of the calcined and used catalysts, where it was possible to identify the nickel oxide phase in both calcined catalysts. In addition, after the steam reforming reaction of ethanol, signals corresponding to carbon formation are observed in both materials.
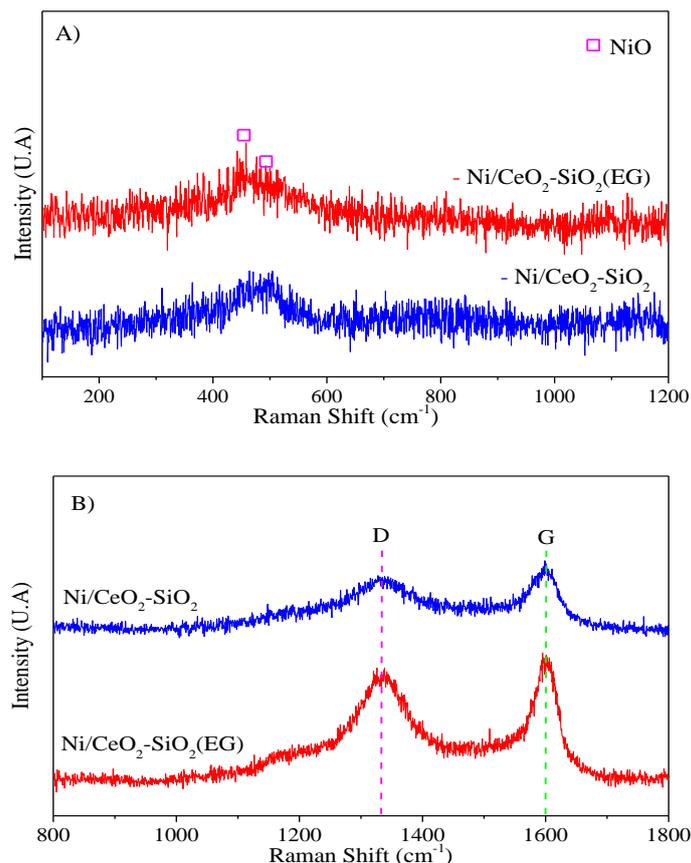

Fig. 4. Raman spectra of A) calcined and B) used in the steam reforming reaction for $Ni/CeO_2-SiO_2(EG)$ and Ni/CeO_2-SiO_2 catalysts. T= 500°C. P=1atm. W/F= $4.9x10^{-3}$ g h L^{-1}.

The X-ray diffraction pattern for the calcined samples are presented in Figure 5, it is observed that neither of the two catalysts showed signals corresponding to the nickel oxide phase, which indicates a very small crystallite size, lower than the detection limit of the technique.
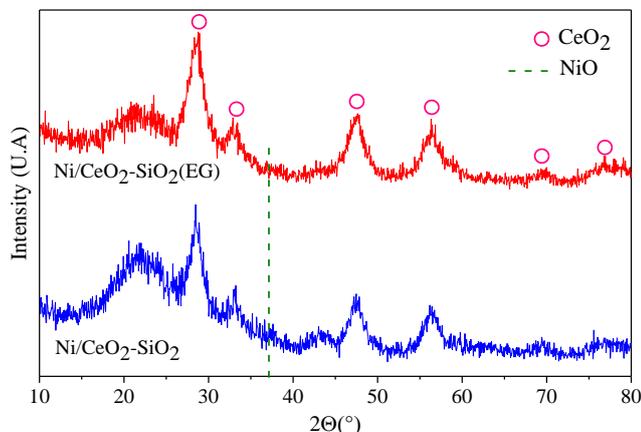

Fig. 5. Diffractograms of calcined Ni/CeO$_2$-SiO$_2$(EG) and Ni/CeO$_2$-SiO$_2$ catalysts.

Signals corresponding to the CeO$_2$ phase are detected, and the crystallite size was calculated by the Scherrer equation to be approximately 3.5 nm in both catalysts. The amorphous halo corresponding to silica is also observed for both materials.

4. Discussion

By pretreatment of the silica with ethylene glycol, it was possible to obtain a more active, stable and selective catalyst for hydrogen production using the steam ethanol reforming reaction. As shown in Figure 1, the Ni/CeO$_2$-SiO$_2$(EG) catalyst maintained 100% conversion during the first 3 h of reaction, decreasing only an 8% after 7 h. On the contrary, the unfunctionalized catalyst showed an initial conversion of 76%, which significantly decreased to 51% after 7 h of reaction.

On the other hand, Figure 2 shows that the hydrogen yield obtained by the Ni/CeO$_2$-SiO$_2$(EG) catalyst in the ethanol steam reforming reaction was 57% higher than that of the unfunctionalized material, indicating its high selectivity towards H$_2$ production. These results are related to the absence of oxygenated compounds such as ethylene and acetaldehyde in the reaction stream for the Ni/CeO$_2$-SiO$_2$(EG) catalyst. In addition, for the unfunctionalized catalyst, the hydrogen yield shows a higher decrease due to the presence of a much higher percentage of acetaldehyde from the beginning of the reaction.

On the other hand, by Raman spectroscopy it was possible to observe the presence of nickel oxide phases in the two catalysts. However, the XRD results suggest a smaller NiO crystallite size in comparison with the cerium oxide, whose size remained around 3.5 nm.

The reduced crystallite size obtained would also favor the activity and stability of these solids in the ESR reaction.

5. Conclusions

By pretreatment of silica with ethylene glycol it was possible to synthesize catalysts that were more active, stable and selective towards hydrogen production in the ethanol steam reforming reaction.

These results suggest that the use of CeO$_2$-SiO$_2$(EG) binary support could help to control the carbon deposition, improving the catalyst stability. Probably, the carbon species being involved in the reaction mechanism, without covering the active sites. Likewise, it is also suggested that the nature of the Si-OH sites could play an important role in the catalytic behavior of these catalysts.

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