Toluene Steam Reforming over Nickel Based Catalysts

S. Sayas, N. Vivó, J.F. Da Costa-Serra, A. Chica*

Instituto de Tecnología Química (Universitat Politècnica de València-Consejo Superior de Investigaciones Científicas), Avd. de los Naranjos s/n, 46022 Valencia (Spain).

*Corresponding author. Tel.: +34 963 87 70 00-78508; fax: +34 963 87 78 09.

E-mail address: achica@itq.upv.es

Abstract

Steam reforming of toluene (SRT) has been studied initially in eight nickel-based catalysts where nickel (10 wt.%) was incorporated in different supports (olivine, Al_2O_3, MgO, LDH, ZrO_2, CeO_2 and natural sepiolite) by the incipient wetness impregnation method. Among them, nickel catalyst based on sepiolite exhibited a promising catalytic performance, with a high conversion of toluene (16%), high selectivity to hydrogen (68.4%) and low production of undesired by-products (CO, CH_4, ethylene and benzene) at low temperature (500 ºC). On the other hand, the incorporation of Ni in the sepiolitic material by precipitation (PP) has been considered as alternative method to the incipient wetness impregnation method (IWI). PP method allowed to prepare a Ni-based catalyst with a very high activity (conversion of toluene ~100%), high selectivity to hydrogen (73%) and lower production of undesirable by-products (5% CO, 2% CH_4 and 0% C_6H_6) at 575 ºC. In addition, catalytic deactivation due to coke deposition and nickel sinterization was clearly lower for the catalyst synthesized by PP. Characterization by different physicochemical techniques (XRD, TEM, BET surface area, ICP-OES, TPR and EA) showed that PP method allowed to obtain a sepiolite-based catalyst containing Ni with larger external surface area and smaller, highly dispersed and easily reducible Ni metal particles. The results here discussed show that the Ni incorporation method has a clear influence in the preparation of nickel catalyst supported on sepiolite with improved catalytic performance in the steam reforming of toluene.

Keywords: Nickel Catalysts, Steam Reforming, Hydrogen Production, Natural Sepiolite, Toluene.

1. Introduction.

Humanity lives in an era characterized by constant changes and challenges from the environmental point of view. There is a real call led by the youths that requires many changes in society at all levels in order to minimize CO_2 emissions and try to mitigate the possible effects of climate change. Focusing on the energetic technologies which are currently being developed, hydrogen could be an excellent alternative fuel on the near future since it can be produced from renewable energy sources and its combustion produces only water as by-product [1]. One of the most important aspects to a hydrogen-based energy system is where the feedstock is coming from, since hydrogen is not a source of energy. Currently, the most part of the hydrogen produced industrially comes from natural gas reforming, a non-renewable feedstock that even favor the Greenhouse Effect, because this technology generates CO_2. Thus, it could be preferable to produce hydrogen from renewable sources [2]. For this reason, currently, biomass emerges as an important source to produce clean and renewable hydrogen, behaving as an excellent eco-friendly hydrogen reservoir. It is not in vain that biomass represents around 10-14% of the world's total energy today [3, 4]. Biomass gasification is one of the most promising processes to obtain hydrogen due to its undoubted advantages. Among its many advantages, the highlight is that biomass gasification is a fast, very efficient and environmentally friendly and renewable process [5]. Biomass gasification consists in a mature technology pathway that uses a controlled process involving heat, steam, and oxygen to convert biomass to hydrogen and other products, without combustion. It should be noted that the origin of biomass for the gasification process can be very varied, especially it can come from forest, agricultural and municipal solid waste. Mainly from the biomass gasification process, three product ranges can be obtained, such as gases (H_2, CO, CO_2, and light hydrocarbons), solids (ashes and chars) and topping atmosphere residue (TAR). TAR consists of cyclic and polycyclic aromatic hydrocarbon compounds such as benzene, toluene and naphthalene [6, 7]. The formation of the above compounds entails a series of drawbacks in the biomass gasification process, such as loss of yield, hazard to the equipment downstairs, reduction gasification performance, and increment in equipment maintenance requirements. For the above reasons, removal of biomass tars is highly desirable. One possibility to solve this problem comes from steam reforming of TAR compounds. Steam reforming of biomass derived compounds (renewable sources) is of great interest due to economic and environmental issues [8-10]. In the literature the use of toluene as a building block to study

in steam reforming of TAR is widespread [11-26]. Steam reforming of toluene reaction produces mainly hydrogen, carbon monoxide, carbon dioxide and benzene. Several side reactions such as dealkylation reaction of toluene by water, water-gas shift, methanation, and Boudouard reaction, among other, may occur in the steam reforming of toluene [27-29]. Thus, the use of catalyst results an interesting option to decrease the production of TARs and increase the selective production of hydrogen. Over the years, the catalysts used in the steam reforming of TARs have been based primarily on transition metals. Nickel supported on oxides can be highlighted among these transition metals [30-43]. Specifically, a variety of works have focused on the study of Ni catalysts supported in alumina such as Ni/gamma-Al_2O_3-SiO_2 with different silicon precursors [44], nickel catalysts supported on hexaaluminates [45], Ni-doped γ-Al_2O_3 [46], Ni/Ce-Al_2O_3 [47], etc. As mentioned, the alumina is one of the most used supports, but it is not the only one. Other types of supports such as SBA-15, graphitic mesoporous carbon (GMC), dolomite, LDH, biochar and olivine have been studied as Ni catalysts [12, 14, 32, 48-50]. These are just some examples of the great variety of supports used in this type of studies. What is no longer so common is that in the same study a great variety of supports and two methods of synthesis of catalysts are analyzed. The work presented in this paper is based on the use of Ni based catalyst supported on eight different supports (olivine, Al_2O_3, MgO, LDH, ZrO_2, CeO_2 and natural sepiolite) as an alternative to precious metals (Pt, Pd, Rh, Ru, etc..), which are most expensive. As it is known that Ni has an optimal performance at moderate temperatures, the substitution of precious metals by Ni could imply a huge progress from an economic point of view. Ni has an optimal performance in the steam reforming of biomass-derived compounds since the C-C bond scission is favored [51, 52]. An optimal catalytic performance is determined by three main parameters: activity, selectivity, and stability of the catalyst. A multitude of factors around the catalyst can affect its catalytic performance such as the selected active metal phase, the precursor used, the chosen support, the catalyst synthesis method, the operating conditions and the presence of additives. Among the mentioned factors, support is a key factor to be considered. In particular, support is crucial to synthesize catalytic materials with high activity, selectivity and stability in the reforming reaction because it can increase the dispersion of the active metal phase and the interactions metal-support, leading to an improvement of the catalytic performance [53, 54]. Together to the support another crucial factor is the method used to incorporate the metallic active phase in the support. Specifically, how the incorporation of the metal phase into the support is carried out influences the performance of the steam reforming catalysts [51]. Depending on the method chosen, high dispersions of the metal phase and strong support-metal interactions can also

be favored. Supports with high BET surface area seem to favor high dispersions of the metallic active phase and promote adequate metal-support interactions [51, 54]. In addition, supports with acidic characteristics would favor the formation of ethylene (coke precursor), deactivating the catalyst by coke deposition [51-54]. Thus, in this paper we have carried out initially a catalytic screening in the steam reforming of toluene of eight nickel-based catalysts where the Ni was incorporated in different supports by incipient wetness impregnation method. In addition, the influence of the nickel incorporation method has been studied using the most promising support selected from the initial catalytic screening. The results obtained show that the Ni incorporation method has a clear influence on the activity, selectivity and stability of the catalysts because it allows to put differences in size, dispersion and reducibility of the supported metallic nickel particles.

2. Experimental.

2.1. Preparation of catalysts.

Olivine, Al_2O_3, MgO, Layered Double Hydroxides (MgLa-LDH and CaAl-LDH), ZrO_2, CeO_2 and natural sepiolite have been used as Ni support. Ni was incorporated on these supports by incipient wetness impregnation (IWI) using an aqueous solution containing $Ni(NO_3)_2 \cdot 6H_2O$ (98%, Sigma-Aldrich). The amount of Ni in the final catalyst was 10 wt.%. After the Ni incorporation catalysts were calcined at 600 ºC for 3 h in a muffle oven. The obtained catalysts were labeled as follow: 10Ni/Olivine, 10Ni/MgO, 10Ni/NS, 10Ni/MgLa-LDH, 10Ni/ZrO$_2$, 10Ni/CeO$_2$, 10Ni/CaAl-LDH and 10Ni/Al$_2$O$_3$. Precipitation method (PP) was also used for Ni incorporation in sepiolite support following the procedure described in [55] with several modifications. Specifically, two solutions were required, first solution contains $Ni(NO_3)_2 \cdot 6H_2O$ (98%, Sigma-Aldrich) and HNO_3 to achieve a pH of 2. The second solution contains the natural sepiolite. First solution was added to the second one using a syringe pump (Kd Scientific) under agitation. Final pH of the solution was adjusted with NaOH to achieve a value of 11. After the solution is filtered, the recovered sepiolite containing the Ni is dried at 100 ºC for 3 hours and calcined in muffle oven at 700 ºC for 3 h. Sample prepared by precipitation method was labeled as 10NiNS.

2.2. Characterization techniques.

Ni content was determined by inductively coupled plasma with optical emission spectrometer (ICP-OES) in a Varian 700-ES Series. Textural properties (BET area and pore volume) were measured using an ASAP 2420 apparatus (Micromeritics) at 77 K. Before the analysis, 200 mg of each pelletized sample (0.25-0.40 mm) were degassed at 673 K with high vacuum ($\sim 5 \times 10^{-6}$ bar) overnight. The BET surface area was calculated by using the Brunauer−Emmett−Teller equation. X-ray diffraction patterns were obtained at room temperature in a Philips X'pert diffractometer using monochromatized CuKα radiation. Micrographs were recorded by Transmission electron microscopy (TEM) using a Philips CM-10 microscope operating at 100 kV. Temperature programmed reduction (TPR) were carried out to study the reduction properties of supported nickel. Measurements were carried out in a Micromeritics Autochem 2910 equipment. Between 30 and 100 mg of sample, in the granulometry 0.25-0.40 mm were loaded in a quartz U-tube to form a fixed bed between quartz wool. Samples were treated in Ar flow at room temperature for 30 minutes and then the circulating gas was replaced with 10% H_2 (vol)/Ar (50 mL/min) and the temperature was increased from room temperature to 1173 K at a rate of 10 K/min. Downstream of the reactor, a 2-propanol/N_2 (l) trap was placed to retain the water formed in the reductions, and H_2 consumption was recorded on a thermal conductivity detector (TCD), previously calibrated using the reduction of CuO as a reference. The amount of carbon deposited in the catalysts after steam reforming reaction was determined by elemental analysis using a Carlo Erba 1106 analyzer. The active metallic surface area was estimated from H_2 adsorption using the double isotherm method on a Quantachrome Autosorb-1 equipment. Prior to adsorption, the samples (ca. 0.3 g) were pre-treated in flowing He at 393 K for 1 h and then reduced in situ by flowing pure H_2 at 973 K for 3 h. After reduction, the samples were degassed and cooled to 373 K to register the adsorption isotherm.

2.3. Catalytic study.

Steam reforming experiments (SRT) were carried out in a continuous fixed bed reactor at atmospheric pressure, H_2O/Toluene molar ratio of 18, contact time = 1 h and reaction temperatures between 400 and 700 °C with a previous reduction step with hydrogen (100 ml·min^{-1}) for 2 hours at 700 °C.

Typical catalytic test consisted in a load of the reactor with 0.5 g of catalyst (grain-size: 0.25-0.42 mm), diluted with the required amount of carborundum (SiC) (grain-size: 0.60-0.80 mm) to achieve a catalyst bed of 5 cm^3.

Reaction compounds were analyzed online using gas chromatography. Chromatograph (Varian 3800) includes two detectors [thermal conductivity (TCD) and flame ionization (FID)] and two columns (TRB-5, L = 30 m, DI = 0.25 mm; CarboSieve SII, L = 3 m, DI = 2.1 mm).

Toluene conversion and products selectivity were determined according to the equations (1) and (2), where $(F_{TOL})_0$ is the flow of toluene fed to the reactor (mol·s^{-1}), $(F_{TOL})_f$ the flow of toluene that comes from the reactor and F_j the flow of product j that comes from the reactor. Selectivity values were calculated as the molar percentage of the products obtained, excluding water.

$$X_{TOL}\ (\%, mol) = \frac{(F_{TOL})_0 - (F_{TOL})_f}{(F_{TOL})_0} \times 100 \ (1)$$

$$S_j\ (\%, mol) = \frac{F_j}{(\Sigma F_j)_{products}} \times 100 \ (2)$$

3. Results and discussion.

3.1. Catalytic activity.

Considering the large variability of the catalytic support published in literature in the steam reforming of toluene we decided to carry out initially a brief catalytic test using different supports containing 10 wt.% of Ni in order to localize a promising support. Alumina-based catalyst was used as reference support. Nickel was incorporated in all the supports by incipient wetness impregnation (IWI) method. Catalytic activity and products selectivity at 500 ºC are shown in Table 1. As it can be seen, sepiolite-based catalyst exhibits similar conversion of toluene than the reference catalysts based on alumina. On the other hand, sepiolitic catalyst shows a larger production of hydrogen and a smaller production of non-desired compounds (CO, CH$_4$ and benzene). Nevertheless, the production of CO by this catalytic material, and especially the benzene production, is considered very high for the properly use of the produced hydrogen in a PEM fuel cell. Thus, hydrogen yields should be increased while the production of benzene and CO should be avoided. To achieve the objectives an alternative method to incorporate Ni in the sepiolitic material was evaluated, precipitation method (PP) [55].

Table 1. Conversion of toluene and selectivity of products in toluene steam reforming for the preliminary catalysts studied in this work. (Reaction conditions: T: 500 ºC, atmospheric pressure, contact time = 1 h and H_2O/Toluene = 18).

Catalyst	Toluene Conv. (mol%)	Products Selectivity (mol%)				
		H_2	CO	CH_4	CO_2	C_6H_6
10Ni/Olivine	1.7	49.6	2.3	0.0	48.1	0.0
10Ni/MgO	0.6	58.3	0.0	0.0	41.8	0.0
10Ni/NS	8.3	68.4	6.6	0.2	16.5	8.3
10Ni/MgLa-LDH	1.5	68.0	0.0	2.0	28.2	1.8
10Ni/ZrO₂	4.5	63.7	16.2	0.2	9.3	10.6
10Ni/CeO₂	0.5	20.2	0.0	36.8	43.0	0.0
10Ni/CaAl-LDH	2.2	72.5	1.9	0.1	20.0	5.6
10Ni/Al₂O₃ (ref)	8.7	63.4	7.7	0.3	14.8	13.8

Steam reforming of toluene was carried out in the temperature range 400-700 ºC with a steam/toluene molar ratio of 18 and a contact time defined as the ratio between the mass flow rate of toluene and mass of catalyst of 1 h. Figure 1a and 1b show the conversion of toluene and the selectivity to hydrogen. As it can be seen, catalytic activity was significantly higher for the catalyst prepared by PP (10NiNS). It seems that PP method allow to prepare an improved sepiolite-based catalyst, with high activity in the steam reforming of toluene. Particularly, higher toluene conversion values and selectivity to hydrogen were detected at lower reaction temperatures (<600 ºC) for the sample prepared by PP. Interesting results are also presented in Figure 1c, 1d and 1e where the distribution of reaction products are shown. As it can be seen, lower concentrations of CO, CH_4, and benzene are also obtained with the sepiolite-based catalyst prepared by PP. To explain the differences found in the catalytic performance exhibited by the sepiolite-based catalysts prepared by PP and IWI, their physicochemical characterization was carried out using different characterization techniques.
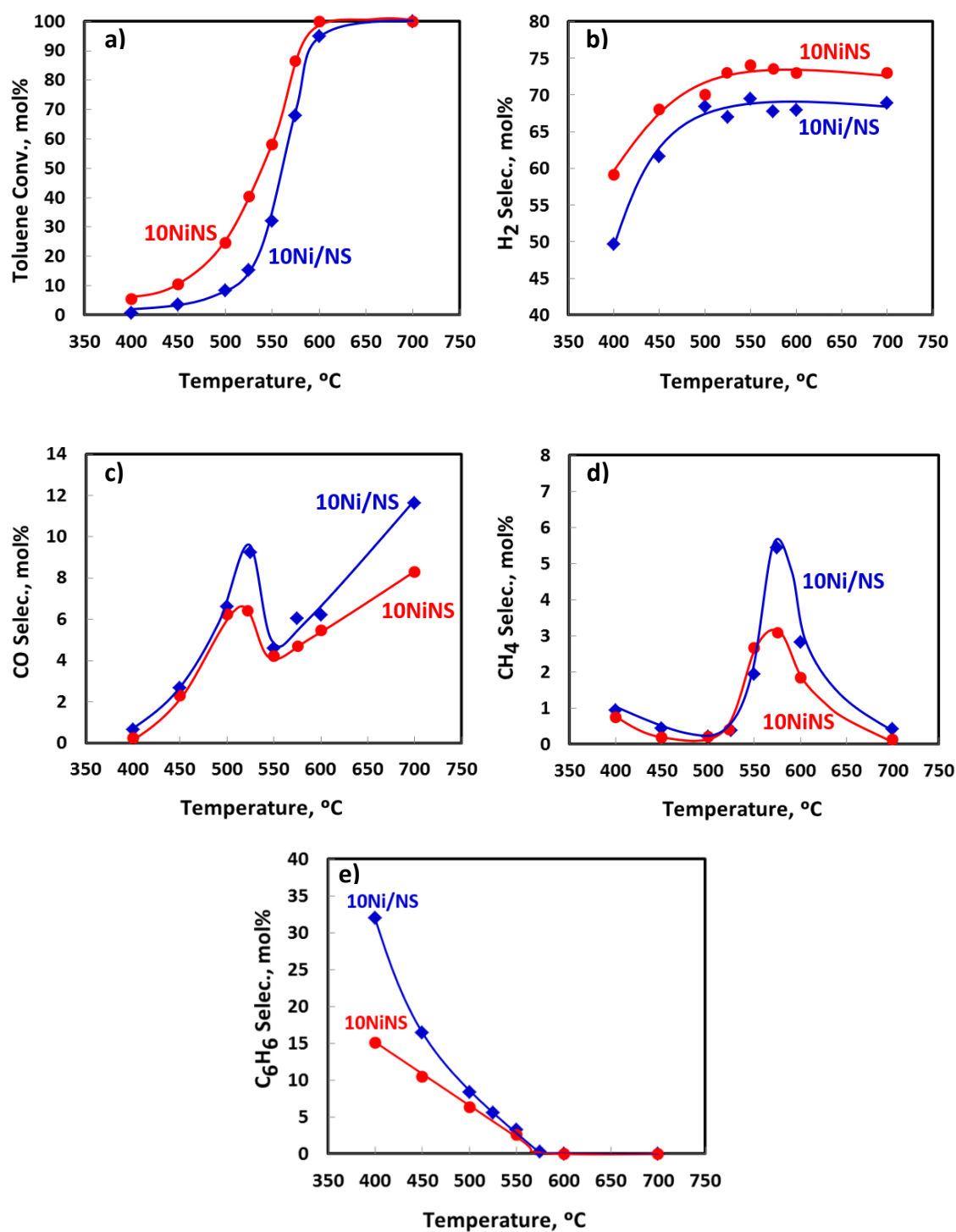
Figure 1. Variation of the toluene conversion (a), hydrogen selectivity (b), CO selectivity (c), CH$_4$ selectivity (d) and benzene selectivity (e) with reaction temperature for the two final catalysts studied in this work. (Reaction conditions: atmospheric pressure, contact time = 1 h and H$_2$O/Tol = 18).

3.2. Catalyst characterization.

BET surface area for the natural sepiolite as it was supplied and for the 10NiNS and 10Ni/NS catalysts after calcination at 700 ºC are shown in Table 2. The calcination step leads to a loss of surface area as it can be deduced from the surface area values determined for sepiolite-based catalysts. The sample prepared by PP presents a surface area slight larger than the sample prepared by IWI. However, the differences found do not seem enough to explain the catalytic results obtained in the steam reforming of toluene.

Table 2. Ni content, BET surface area, metallic Ni crystallite size determined by XRD and TEM, metallic Ni surface area, dispersion and reducibility % at 700 ºC for the catalysts studied in this work.

Sample	Ni, (wt.%)	BET area (m²/g)	Ni⁰ Size, XRD (nm)	Ni⁰ Size, TEM (nm)	Active Ni⁰ surface area, (m²/g)	Ni⁰ dispersion, (%)[a]	Reducibility %, (700 ºC)
Sepiolite	-	157	-	-	-	-	-
10NiNS	8.9	113	8	7	8.4	14.4	86
10Ni/NS	9.1	107	12	13	5.7	7.8	47

(a) Calculated from dNi(nm) = 101/D(%) [51], D: dispersion and dNi(nm): size of the Ni metallic particle determined by TEM.

X-ray diffractograms (XRD) for natural sepiolite (NS) as it was supplied and for catalysts prepared by IWI (10Ni/NS) and PP (10NiNS) calcined at 700 ºC are presented in Figure 2a. It is clear that sepiolite structure is lost after calcination. For calcined catalysts it can be seen different peaks at 37.3º, 43.2º, and 62.8º related to the presence of NiO (JCPDS 22-1189) and at 74.9º and 78.8º could be related to the presence of MgNiO$_2$ (JCPDS 24-0712). XRD of the reduced catalysts is also presented in Figure 2b. As it can be seen, the peaks corresponding to oxidized nickel disappear and metallic Ni diffraction peaks appear at 44º, 51.8º, and 76.5º (JCPDS 00-004-0850). From these peaks, the size of the metallic nickel particles has been determined using the Scherrer equation [56]. Lower average size was found for catalyst prepared by PP (8 nm and 12 nm for IWI). TEM was also used to determine the size of the metallic Ni particles (Figure 3), finding similar results to those determined by XRD, Table 2. Nevertheless, the distribution of sizes seem to be higher for the

catalyst prepared by IWI (10Ni/NS), indicating that IWI method produces a distribution of sizes more heterogeneous, with a larger percentage of metallic particles with a large size than PP method (7.8% and 24.9% of metallic particles with sizes >15 nm, respectively).
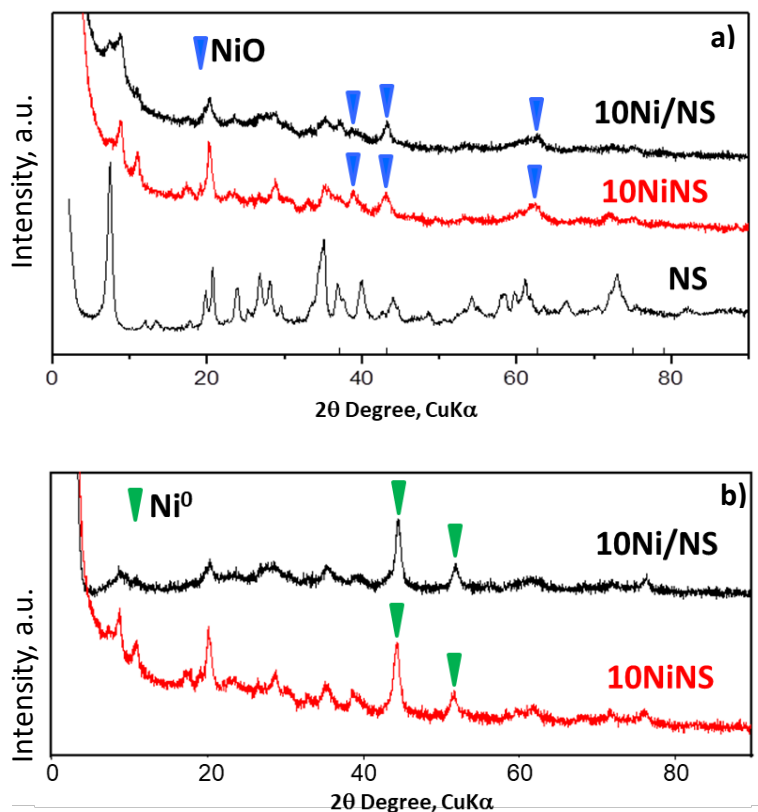
Figure 2. a) XRD of natural sepiolite as it was supplied and calcined 10NiNS and 10Ni/NS catalysts at 700 ºC. b) XRD of reduced 10NiNS and 10Ni/NS catalysts at 700 ºC.

This observation is very important considering that differences in surface area are not significant. Considering the similar surface area presented by both samples, the presence of smaller metallic Ni particles in the sample prepared by PP (10NiNS) would involve a larger number of active metallic sites available for steam reforming reaction, explaining the higher catalytic activity presented by this sample [53, 57]. This hypothesis is confirmed with the data obtained by H_2-chemisorption shown in Table 2. As it can be seen, the active metal surface area determined for the sample prepared by PP (10NiNS) was clearly higher (8.4 m^2/g and 5.7 m^2/g), explaining the higher catalytic activity presented by this catalyst.
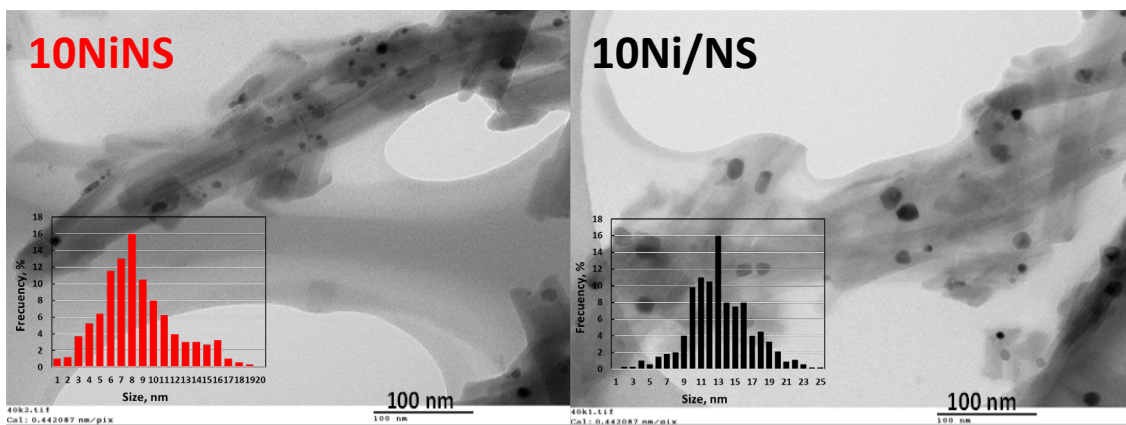
Figure 3. TEM images of reduced catalysts.

The smaller size of the metallic Ni particles and the higher active metal surface area present in the catalyst prepared by PP could be related to the Ni incorporation method. PP method could be providing better positions in the sepiolitic material to accommodate and stabilize the metallic particles of Ni, avoiding their sinterization during the calcination and reduction steps and explaining the smaller size detected for this sample. To corroborate this hypothesis reduction behaviors of the nickel incorporated by PP and IWI have been studied by temperature programmed reduction (TPR). As it can be seen in Figure 4, the reduction profile of the sample prepared by IWI (10Ni/NS) presents three main reduction peaks at 435 ºC, 495 ºC and 715 ºC, related to the reduction of bulk NiO [51, 53, 58-65], $NiO-SiO_2$ [66] and NiO-MgO in the surface [67], respectively. In the case of the catalyst prepared by PP (10NiNS) it can be found also four main reduction peaks at 453 ºC, 510 ºC, 704 ºC and 813 ºC related to the reduction of bulk NiO [51, 53, 58-65], $NiO-SiO_2$ [66], surface NiO-MgO and NiO-MgO in the bulk [67], respectively. The reduction degree of the Ni supported on sepiolite at 700 ºC has been also determined, finding a higher reducibility for the sample prepared by PP (86% for 10NiNS and 47% for 10Ni/NS). This result suggests that a larger amount of metallic nickel would be present in this catalyst. In addition, it has been detected also for this sample a higher intensity of the reduction peaks related to bulk NiO (peak at 453 ºC) and NiO interacting with MgO in the surface (peak at 704 ºC), what could be explained by the larger active metal surface area determined by H_2-chemisorpton for this sample.

As conclusion of this study, it can be said that the differences found in the reduction studies and in the size of the metallic Ni particles seem to be related to the different methodology used to incorporate the Ni in the

sepiolitic support. PP method seems to favor the stabilization of supported Ni, facilitating their dispersion

and reduction and avoiding their sinterization during the successive calcination and reduction steps.
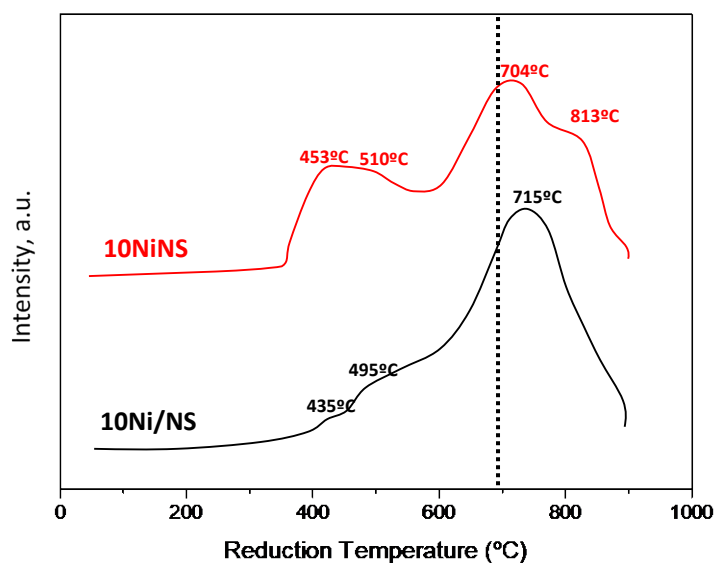
Figure 4. TPR of calcined catalysts. Dotted line corresponds to the temperature used for the reduction of

the catalyst before reaction.

3.3. Deactivation studies.

Catalytic stability is an important issue to be considered for the proper performance of a catalyst. Stability

is related to the deactivation of the catalyst with reaction time, which can be related with the formation of

carbon deposits and sinterization of the metallic particles [52, 57, 68]. Table 3 shows the catalytic activity

of the 10NiNS and 10Ni/NS samples after 5 and 24 h of reaction time. As it can be seen, deactivation occurs

in a larger extension in the catalyst prepared by IWI. Elemental analysis after reaction shows that the

deposited coke was higher for this sample (Table 3), supporting the larger deactivation detected.

Table 3. Conversion of toluene, deposition of carbon and size and level of sinterization of the metallic nickel particles. Data obtained after 24 hours of reaction time. Reaction conditions: H_2O/Toluene =18 (mol/mol), contact time = 1 h, 575 °C and atmospheric pressure.

Catalyst	%Conv. 5h	%Conv. 24h	Carbon (wt.%)	Ni^0, XRD (nm)	Sinterization, (%)
10NiNS	87.8	86.6	16.0	10	25
10Ni/NS	70.4	63.2	26.0	20	67

XRD of the spent catalysts was also carried out, (Figure 5). The existence of NiO has been detected for the catalyst prepared by IWI. The presence of oxidized nickel (NiO) indicates that part of the metallic nickel has been reoxidized during the steam reforming of toluene. This reoxidation does not seem to occur in the catalyst prepared by PP. Oxidized nickel is not active in the reforming reaction, thus, it would be cooperating in the loss of activity observed for this sample after 24 h of reaction. From XRD of the spent catalysts the size of the Ni metallic particles was determined also using the Scherrer equation [56]. As it can be seen in Table 3 the sinterization level was significantly lower for the sample prepared by PP. Thus, carbon deposition, nickel oxidation and sinterization of metallic Ni particles would be contributing for higher deactivation level detected in the catalyst prepared by IWI (10Ni/NS).
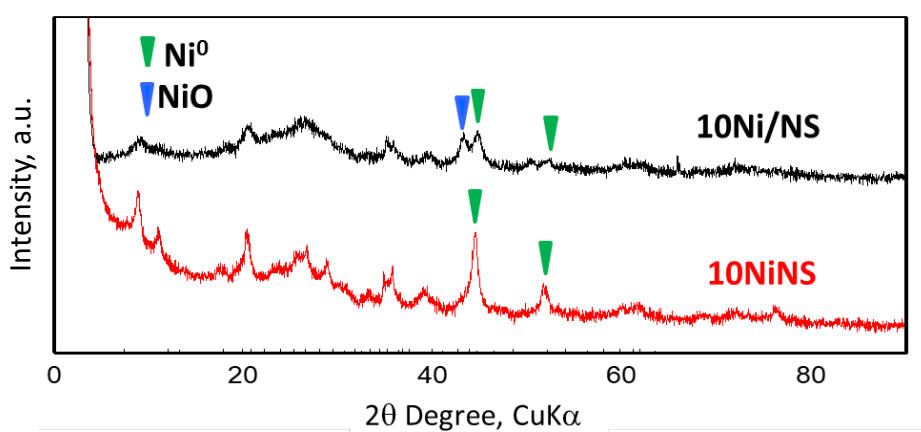
Figure 5. XRD of spent catalysts after steam reforming of toluene. Data obtained after 24 hours of time of stream. Reaction conditions: H_2O/Toluene =18 (mol/mol), tc = 1 h, 575 °C and atmospheric pressure.

The results presented here show that the Ni incorporation method is of paramount importance to prepare a catalyst based on nickel supported on natural sepiolite with improved catalytic activity in the SRT. Specifically, it has been shown that the incorporation of Ni by the precipitation method (PP) allows to prepare smaller metallic particles of nickel, highly dispersed and more accessible for the steam reforming of toluene. In particular, PP method has allowed to prepare a Ni-based catalyst supported on sepiolite highly active and selective to hydrogen and with improved resistance to deactivation due to lower coke deposition and lower oxidation and sinterization of their metallic Ni particles.

4. Conclusions.

Several supports promoted with Ni have been tested in the steam reforming of toluene (SRT). The catalytic performance of the different materials prepared by incipient wetness impregnation (IWI) are quite diverse, confirming the importance of the selection of the support to prepare catalysts with high activity in the SRT. Sepiolite-based catalyst exhibited a promising catalytic performance, with high catalytic activity, high selectivity to hydrogen and low production of undesired by-products (CO, CH_4 and benzene). In order to optimize the incorporation of the Ni in the sepiolitic support an alternative method has been studied (precipitation method, PP). Catalytic results show that precipitation allows to prepare a Ni-sepiolite-based material 10NiNS with improved catalytic behavior in the SRT. Physicochemical characterization of the sepiolitic catalysts was carried out to explain the differences found in the catalytic studies. Obtained data suggests that the higher reducibility, smaller size of the metallic Ni particles and the higher active metal surface are the main responsible of the enhanced catalytic performance exhibited by the sample prepared by PP (10NiNS). In addition, this sample presented a lower deactivation, that seems to be related to the lower coke deposition and lower oxidation and sinterization of the metallic Ni particles. Therefore, it has been proved that the method of the incorporation of Ni in sepiolitic supports is critical to prepare a highly active, selective and stable catalyst in the SRT.

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