Ni-doped γ-Al_2O_3 as secondary catalyst for bio-syngas purification: influence of Ni loading, catalyst preparation and gas composition on catalytic activity

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Abstract

In this work, Ni/γ-Al_2O_3 catalysts were prepared by sol-gel methods with different Ni loadings (10 to 50 wt.%) and used as secondary catalyst for the steam reforming of toluene. A sample prepared by wet impregnation with 10 wt.% of Ni was also synthesized and compared to the corresponding sol-gel sample. This study was divided in three main parts: the comparison of catalysts prepared by sol-gel process and impregnation, the influence of the gas composition on the catalytic performance of the sol-gel 10 wt.% Ni/γ-Al_2O_3 catalyst and the influence of Ni loading on the catalytic activity.

When sol-gel and impregnated samples are compared, the impregnated catalyst showed a high initial toluene conversion followed by a consequent and progressive deactivation. Contrarily, the sol-gel catalyst showed a stable catalytic activity and relatively low carbon deposit. Indeed, before the steam reforming of toluene at 650 °C, the sol-gel catalyst was only calcined and no reduction step was realized to reduce nickel oxide. So this sample was reduced during the catalytic test at 650 °C. Moreover, it was observed that, if toluene was withdrawn from the syngas mixture during the catalytic test, the sol-gel sample was progressively re-oxidized by CO_2 and H_2O, leading to higher deactivation.

As the Ni loading increased, the nickel oxide with strong interactions ($NiAl_2O_4$) was progressively joined by nickel oxide with low interactions (NiO/Al_2O_3) and bulk nickel oxide (NiO). This led to a high initial conversion of toluene, but also to a progressive loss of the catalytic activity throughout the catalytic test. It was shown that the sol-gel method developed throughout this work allowed preparing micro/mesoporous $Ni/\gamma\text{-}Al_2O_3$ catalysts with a high dispersion of Ni nanoparticles.

1. Introduction

Nowadays, the biomass gasification appears as an interesting and versatile way to take advantage of different energy sources (*e.g.* agricultural and urban wastes, energy crops, food and industrial processing residues). If managed conscientiously, these processes can therefore lead to the sustainable and renewable production of a bio-syngas, which can either be used directly as combustible or converted into storable and high valuable chemical compounds such as methanol [1, 2]. However, despite the fact that bio-syngas is predicted to be an economically viable energy and that some industrial plants are already in action, bio-syngas technologies still encounter some technical problems, which seriously hinder their commercial development [3, 4]. Indeed, in practical applications, there are still some technical problems due to high tars concentration in the outlet gas which can condensate and clog the pipes. Modifications of the gasifier reactor design and of the gasification operating conditions (temperature, space ratio, gasifying reagent) have proved to substantially reduce the tar concentration [5–9].

Many studies have highlighted the fact that the tar elimination via catalytic reforming seem to be the more practical and economical solution [3, 9–15]. The required properties of the catalysts are determined by its location: inside the reactor (primary catalyst) or outside the reactor (secondary catalyst). Primary catalysts are generally robust, non-toxic, cheap materials and they are almost only intended for fluidized bed reactors. Secondary catalysts are more versatile and can be used at the exit of both fluidized and fixed bed reactors. They are characterized by tailored mesoporous shapes, controlled active site dispersions and adapted elemental compositions. This work was focused on designing materials for secondary catalytic applications, *i.e.* working at relatively low temperature (~ 650°C) with no mechanical stress.

Among the entire metallic elements commonly used as catalysts, transition metals are the more recurrent. By definition, a transition metal is a metal that forms one or more stable ions which has not completely filled its *d* orbital. This particularity enables them to change their oxidation states and therefore to easily lend or take electrons from other molecules. The metallic active states possess a greater capacity to decompose tars in the produced gas in comparison to the oxidized states [16–18].

Although widely used industrially, Ni is not the most effective catalyst for steam reforming. However, it is the element showing the most interesting activity/price ratio compared to other more precious metals such as Ru or Rh [3]. The optimum Ni loading is situated around 15 wt.% for impregnated and 20 wt.% for precipitated catalysts [9].

These catalysts are commonly supported on Al_2O_3, ZrO_2, Zeolites or Olivine. Various studies agree on the fact that γ-Al_2O_3 seems to be the best support for secondary catalyst applications [10, 15, 17, 19, 20] thanks to (i) its large specific surface area (200-500 m^2/g), (ii) a high mechanical strength and (iii) a good sintering resistance. The two most common preparation methods for Ni/γ-Al_2O_3 catalysts are the incipient wetness impregnation and the sol-gel process. It appears that due to weaker active site/support interactions, the metallic nanoparticles from impregnated catalysts are more inclined to sinter and undergo coke deactivation, especially by carbon whiskers formation. Although generally showing a lower activity, sol-gel synthesized catalysts are more interesting in terms of lifetime [3, 21–23].

In this work, Ni/γ-Al_2O_3 catalysts will be prepared by a new aqueous sol-gel methods with different Ni loadings (10, 20, 30 and 50 wt.%) and will be compared for the reforming of toluene as secondary catalyst. A sample prepared by wet impregnation with 10 wt.% of Ni will be also prepared and compared to the corresponding sol-gel sample.

The aims of this work will be to study the influence of the Ni loading and the catalyst preparation method on the catalysts performances and lifetime with a newly developed sol-gel synthesis. It will allow to assess which sample better resist to sintering and coke deactivation. Another aim of this manuscript will be to understand the influence of the syngas composition on the performances of these new catalysts. It is why the same catalyst will be tested with different gas conditions: (i) syngas without CH_4; (ii) syngas without toluene; (iii) syngas with toluene only for the first 105 min of test and (iv) syngas without neither toluene nor CH_4.

2. Materials and Methods

2.1. *Ni/γ-Al_2O_3 catalysts prepared by sol-gel method*

The sol-gel prepared Ni/γ-Al_2O_3 catalysts were synthesized according to a synthesis procedure described in [24]. First, aluminum precursor (aluminum nitrate, $Al(NO_3)_3.9H_2O$, ≥ 98%, Sigma Aldrich) and water are mixed together. Then, the sols were formed by a slow addition of a NH_4OH solution (30 wt.%, 15 M). After precipitation, the sols were agitated for 24 h at 85 °C, washed two times with water, re-dispersed in water and nickel nitrate hexahydrate

($Ni(NO_3)_2.6H_2O$, 99.99%, Sigma Aldrich) was added. The sols were stirred for 30 min. The doped sols were put in an oven for aging (24 h, 85 °C, 700 mbar) and for drying (24 h, 110 °C, 900 mbar). The dried gels were calcined for 5 h at 550 °C, with a heating rate of 2 °C/min. Ni10/Al_2O_3, Ni20/Al_2O_3, Ni30/Al_2O_3 and Ni50/Al_2O_3 samples were prepared according to this procedure with loadings of respectively 10, 20, 30 and 50 wt.% of Ni (Table 1).

2.2. Ni/γ-Al_2O_3 catalysts prepared by impregnation method

Ni10/Al_2O_3-IMP sample was prepared by a wet impregnation method. The support consisted of calcined *γ*-Al_2O_3 synthesized according to the procedure used for the preparation of Ni-doped samples but without Ni. The support was crushed and sieved in order to get grain sizes comprised between 300 and 700 μm, which were set in a glass balloon with water and nickel nitrate. The balloon was fixed to a Rotavap apparatus and the water was evaporated under continuous agitation at 85 °C and under 300 mbar. The dried sample was thereafter calcined with similar calcination procedure as for sol-gel Ni-doped samples (5 h at 550 °C).

2.3. Characterization of Ni/γ-Al_2O_3 catalysts

Samples compositions are determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES), equipped with an ICAP 6500 THERMO Scientific device. Solid samples are crushed and then dissolved with lithium tetraborate before analysis. Aluminum, nickel, silicon and sodium loadings are obtained by comparison with standard solutions in the same medium.

Textural properties are determined thanks to nitrogen adsorption-desorption isotherms which are measured at -196 °C on a Micromeretics ASAP 2010 instrument after 12 h of outgassing at 300 °C and 10^{-5} Pa. The microporous volume, V_{DR}, is calculated by the Dubinin-Raduskevitch method on the first branch of the adsorption curves at low relative pressure (p/p_0

< 0.4). The pore size distributions are determined by the Broekhoff de Boer method (BdB) applied to the adsorption profil-branch of the nitrogen isotherm [25].

The crystallographic properties of samples are determined by X-ray diffraction on a diffractometer Siemens D5000 (Cu-K_α radiation) between 30° and 80° (2 θ) with a step time of 18 s and a step size of 0.04 s. The alumina crystallites sizes were calculated by using the Scherrer equation centered on the (4 0 0) ray γ-Al_2O_3 (2 θ = 67.0 °) of the XRD pattern. The $Ni^{(0)}$ crystallites sizes were calculated by using the Scherrer equation centered on the (2 0 0) ray (2 θ = 51.83 °).

The sizes of metallic particles and their distribution are measured by transmission electron microscopy (TEM) performed on a CM10-PW6020 Philips Electron Microscope by averaging the measurement of approximately 100 particles on TEM micrographs. First, crushed samples are dispersed in absolute ethanol. Then a drop of the dispersion is placed on a copper grid (Formvar/Carbon 200 Mesh Cu from Agar Scientific).

H_2 reduction steps were performed on 1 g of sample. The reactor was first purged with helium at room temperature (15 min, 50 mL/min), then a hydrogen flux was send to the sample (50 mL/min) and the temperature was increased (from 25 °C to 750 °C with a heating rate of 5 °C/min). After 1 h at 750 °C, the heating was stopped and the reactor was purged with helium (50 mL/min).

Temperature Programmed Reduction measurements were performed with a TPD/R/O 1100 device from CE instruments to give information about the reduction of nickel present in the samples. An amount of 0.2 g of catalyst was put in a tube quartz. Samples were heated from 25 °C to 1000 °C with a heating rate of 2 °C/min and under a flow of 20 mL/min of a gas mixture (5 %vol. H_2 /95 %vol. N_2).

After the catalytic tests, carbon deposits are studied with thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements, which are realized with a Sensys

Setaram instrument. Samples are heated from 25 °C to 800 °C with a heating rate of 2 °C/min under air (20 mL/min).

2.4. Catalytic experiments

The catalytic experiments are performed on an experimental toluene reforming installation whose schemes are presented in Figures 1 and 2. In order to prevent corrosion, the tubing is in stainless steel (Inox AISI type 316). Each gas line includes a filter (2 µm), an electro-valve, a pressure captor, a mass flow controller and a check valve. Liquid deionized water is injected thanks to a peristaltic pump (ISMATEC, Multi channels). Due to incompatibility between toluene and various polymeric tubes for peristaltic pump, the liquid toluene is injected thanks to a syringe pump (KDScientific, Legato) and a syringe made of glass and PTFE. The different gases and liquids are injected and heated in a stainless steel mixing chamber. The mixing chamber and all the downstream tubes are heated at 180 °C in order to prevent any water or toluene condensation. At the exit of the mixing chamber, the gas mixture is directed either towards the stainless steel reactor or towards the bypass line. The reactor is made of inox 316 with ½ inch intern diameter (Figure 2). Inside the metallic reactor is placed a quartz tube to avoid contact between the reactive gas mixture and the metallic reactor at temperatures higher than 400 °C. Catalytic samples is introduced inside the quartz tube and maintained thanks to two quartz wool layers and a quartz stalk. A PTFE seal is set between the metallic reactor and the quartz tube at the bottom of the reactor. According to the temperature gradient measurements realized on the catalytic reactor of this study (Figure 2), the catalytic samples are placed between 250 and 400 mm from the reactor bottom.

The effluent is analyzed by gas chromatography (GC Compact, Interscience) with different detectors and columns: (i) a FID detector to quantify the organic compounds (CH_4, toluene, benzene) with an analytic column (RTX1) and (ii) a TCD detector for the other gas

(CO_2, CO, H_2, N_2) thanks to a backflush line with two analytic columns (Molsieve 5A and Porapak). It is also possible to quantify H_2O with the TCD detector. For both detectors, He is used as carrier gas.

The catalytic samples were crushed and sieved with a particle diameter distribution between 315 and 700 µm. The standard catalytic tests were performed with a toluene concentration of 24.000 ppmv and with a standard gas mixture: 31.5 %vol. H_2, 31.5 %vol. CO, 15.2 %vol. CO_2, 11 %vol. H_2O, 10 %vol. The mass of the catalyst was set to 300 mg, for a catalytic bed height of h =12 mm, with a gas flowrate of 50 mL/min and consequently a *GHSV* of 5000 h^{-1} (residence time of 0.72 sec). The standard catalytic tests were performed at 650 °C, for 300 min.

The toluene conversion, C_T, is determined from the Equation 1:

$$C_{\mathrm{T}} = \frac{C_{\mathrm{T,In}} - C_{\mathrm{T,Out}}}{C_{\mathrm{T,In}}} * 100 = \frac{M_{\mathrm{T,In}} - M_{\mathrm{T,Out}}}{M_{\mathrm{T,In}}} * 100 \qquad (1)$$

where $C_{T,in}$ is the initial toluene concentration (mol/m^3) and $C_{T,out}$ is the toluene concentration at the outlet of the reactor (mol/m^3); and $M_{T,in}$ is the initial toluene mass (kg) and $M_{T,out}$ is the toluene mass at the outlet of the reactor (kg).

The benzene selectivity (S_B) is determined from the Equation 2:

$$S_{\mathrm{B}} = \frac{C_{\mathrm{B,Out}}}{C_{\mathrm{T,In}} - C_{\mathrm{T,Out}}} * 100 \qquad (2)$$

where $C_{B,Out}$ is the outlet concentration of benzene (mol/m^3), $C_{T,In}$ is the initial toluene concentration (mol/m^3) and $C_{T,Out}$ is the toluene concentration at the outlet of the reactor (mol/m^3).

The methane conversion, C_{CH4}, is determined from the Equation 3:

$$C_{\mathrm{CH4}} = \frac{C_{\mathrm{CH4,In}} - C_{\mathrm{CH4,Out}}}{C_{\mathrm{CH4,In}}} * 100 \qquad (3)$$

where $C_{CH4,In}$ is the initial methane concentration (mol/m^3) and $C_{CH4,Out}$ is the methane concentration at the outlet of the reactor (mol/m^3).

All C_T, S_B and C_{CH4} values were obtained by making an average of the results obtained during the last 10 measurements of each test.

The consumption rate of toluene, r_T (mol$_T$/(g$_{Ni}$.h)), was also compared. For this gas mixture, the (H_2O + CO_2)/C ratio is about 1.6 when only taking toluene as carbon source, and it is about 1.0 when taking toluene + methane as carbon source. Though these values are low, they are equal or higher to the stoichiometric ratio. Hence, the toluene consumption rate can be expressed with respect only to the toluene concentration and according to a first order (n = 1), which leads to:

$$-r_{\mathrm{T}} = k.C_{\mathrm{Tolu}} \tag{4}$$

where r_T is the consumption rate of toluene (mol$_T$/(g$_{Ni}$.h)), k is the apparent kinetic constant (m^3/(g$_{Ni}$.h)) and C_{Tolu} is the concentration of toluene (mol$_{Tolu}$/m^3).

Since the reaction rate is assumed to be of first order (n = 1), r_{Tolu} can also be expressed as follows [26, 27]:

$$r_{\mathrm{T}} = \left(-\frac{F_{\mathrm{T}}}{W}\right) \ln\left(1 - f_{\mathrm{T}}\right) \tag{5}$$

where F_T is the molar flowrate of toluene at the reactor inlet (mol$_T$/h), W is the nickel mass inside the reactor (g) and f_T is the toluene conversion (Equation 1).

The yield of methane, Y_{CH4}, which corresponded to the methane produced from the conversion of toluene by hydrocracking ($C_7H_8+H_2 \rightarrow C_6H_6+CH_4$) or by hydrodealkylation ($C_7H_8+10.H_2 \rightarrow 7.CH_4$) reactions was determined according to Equation 6:

$$Y_{CH4} = \frac{n_{CH4,Out}}{7*n_{\mathrm{T,In}} - (7*n_{\mathrm{T,Out}} + 6*n_{\mathrm{B,Out}})} \tag{6}$$

where $n_{T,In}$ is the initial amount of toluene (mol), and $n_{T,Out}$, $n_{B,Out}$, $n_{CH4,Out}$ are respectively the amounts of toluene, benzene and methane at the exit of the reactor (mol). This yield did not take into account the carbon deposit and could only be used as an estimation value.

In order to get a more accurate comparison of the coking tendency of the catalysts, the term *Coke** was introduced. This value corresponds to the amount of carbon formed by gram of toluene converted and is determined by Equation 7:

$$Coke^{*} = \frac{Coke}{r_{\mathrm{T}} * \left(\frac{\%Ni}{100}\right) * t * M_{\mathrm{T}}} \tag{7}$$

where *Coke* is the amount of carbon deposit determined from TG-DSC measurements ($g_{\mathrm{Carbon}}/g_{\mathrm{Cata}}$), ($\%Ni/100$) is the gram of nickel by gram of catalyst, determined from ICP-AES measurements, r_{T} is the consumption rate of toluene ($\mathrm{mol_{Tolu}}/(g_{\mathrm{Ni}}.\mathrm{h})$), t is the time of test (5 h) and M_{T} is the molecular mass weight of toluene (92.1 g/mol).

The influence of the gas composition will be evaluated on the catalytic activity of $Ni10/Al_2O_3$ sample, this catalyst was tested for 300 min at 650 °C according to the following conditions: i) standard conditions; ii) without methane; iii) without toluene; iv) with standard conditions until 105 min of test, after toluene was removed from the syngas mixture; v) without methane and without toluene. Table 1 shows the composition of the gas mixtures during the catalytic tests.

3. Results and Discussion

3.1. Catalyst composition

Table 2 shows the theoretical and actual compositions of all samples. The theoretical and actual compositions were similar for all samples. No loss of materials was happened during the synthesis, calcination and reduction steps.

3.2. Influences of the catalysts preparation method

3.2.1. Physico-chemical properties of $Ni10/\gamma\text{-}Al_2O_3$ catalysts prepared by impregnation or by sol-gel method

Table 2 shows the textural properties after calcination, and the metallic Ni particles sizes after either reduction step or TPR measurements determined by TEM and XRD analyses for Ni10/Al_2O_3 and Ni10/Al_2O_3-IMP samples. It was observed that the textural properties of Ni10/Al_2O_3-IMP sample slightly decreased compared to Ni10/Al_2O_3 sample (ΔS_{BET} = - 30 m^2/g, ΔV_p = 0.1 cm^3/g), probably because of the impregnation with nickel salts and of the second calcination step. Figures 3a and 3b illustrate the TEM micrographs of Ni10/Al_2O_3 and Ni10/Al_2O_3-IMP samples after reduction step.

After H_2 reduction step, d_{TEM}, σ_{TEM} and d_{XRD} values (Table 2) were relatively similar for Ni10/Al_2O_3 and Ni10/Al_2O_3-IMP sample. On the opposite, after TPR measurement, Ni10/Al_2O_3-IMP sample showed a more important standard deviation compared to Ni10/Al_2O_3 sample (σ_{TEM} = 15 nm *vs* σ_{TEM} = 9 nm) (Table 2). Figure 4 presents the distribution of the metallic Ni particle sizes after H_2 reduction step and after TPR measurement for both samples.

Figure 5 shows the TPR profiles of both samples. In the case of Ni10/Al_2O_3-IMP sample, broad and asymmetric H_2 consumption peaks revealed the presence of different interactions between the Ni oxides and the alumina support. Three types of oxides were observed: i) bulk NiO was present between 400 °C and 550 °C. Bulk NiO is known to share very few interactions with the alumina support. Indeed, at this loading of metal (10 wt.%), bulk NiO is more likely encountered for nickel supported on α-Al_2O_3; ii) NiO/Al_2O_3 was present between 550 °C and 700 °C. In that case, the Ni^{2+} ions are in octahedral coordination and show relatively strong interactions with the support; iii) $NiAl_2O_4$ was observed from 700 °C to 1000 °C [28–30]. In that case the Ni^{2+} ions are in tetrahedral coordination and are fully integrated inside a spinel structure of nickel aluminate [29, 31, 32]. The presence of Ni incorporated into γ-Al_2O_3 is evidenced by the fact that the TPR curve did not come back to the baseline at T = 1000 °C. Indeed, it was estimated for sample Ni10/Al_2O_3-IMP, that only 90 % of the Ni was reduced during the TPR measurement.

On the opposite, Ni10/Al_2O_3 sample (Figure 5) presented only a symmetric and narrow consumption peak, which evidenced the exclusive presence of $NiAl_2O_4$ [30–32]. This observation was in accordance with other studies, in which Ni/γ-Al_2O_3 materials were prepared by a sol-gel method and with similar nickel doping [33–35]. In that case, the TPR baseline came back to zero at $T = 1000$ °C and the reduction of Ni was close to 100 %.

Since both samples presented Ni particles with similar initial sizes and dispersions after the H_2 reduction (Figure 4a) and showed similar textural properties (Table 2), it was deduced that the different type of Ni oxides observed in Ni10/Al_2O_3-IMP and Ni10/Al_2O_3 samples during the TPR measurements was only a consequence of the preparation method. This assumption was strengthened by the fact that previous studies highlighted that nickel/alumina interactions were greatly influenced by the preparation method [31, 33, 35].

3.2.2. Catalytic activity of Ni10/γ-Al_2O_3 catalysts prepared by impregnation or by sol-gel process

Figure 6a shows the evolution of the toluene conversion as a function of time. Table 3 shows the Ni particles sizes and the catalytic performances of Ni10/Al_2O_3-IMP and Ni10/Al_2O_3 samples. Ni10/Al_2O_3-IMP sample showed a high C_T value at the beginning of the test (87 % for the first measurement, Figure 6a), but presented a high loss of catalytic activity during the followed measurements ($\Delta C_T = -26$ %). After 105 min, C_T was relatively stabilized around 50 %, but it seemed that C_T continued to slightly decrease until the end of the test. In the opposite, Ni10/Al_2O_3 sample started with a low C_T value (38 %) but was progressively activated during the test until it reached a stable C_T value (51 %). This sample was not deactivated during the 300 min of test.

It was observed in Table 3 that Ni10/Al_2O_3-IMP sample presented higher catalytic activity values compared to Ni10/Al_2O_3 sample: a higher toluene reforming rate ($r_T = 7.6\ .10^{-2}$

$mol_{Tolu}/(g_{Ni}.h)$ *vs.* $r_T = 6.7\ .10^{-2}\ mol_{Tolu}/(g_{Ni}.h)$), a higher methane conversion ($C_{CH4} = 13$ % *vs.* $C_{CH4} = 10$ %) and a lower benzene selectivity ($S_B = 8$ %, whereas $S_B = 15$ %). However, Ni10/Al_2O_3-IMP sample presented a higher sensibility towards carbon formation than Ni10/Al_2O_3 sample ($Coke = 8.9\ .10^{-2}\ g_{Carbon}/g_{Tolu}$, *vs.* $Coke = 3.1\ .10^{-2}\ g_{Carbon}/g_{Tolu}$).

The analysis of the post-test DSC curves presented in Figure 6b revealed that, whereas the carbon deposit of Ni10/Al_2O_3 sample was only composed of amorphous carbon (burned at $T < 550$ °C), the carbon deposit of Ni10/Al_2O_3-IMP sample was constituted of both amorphous and filamentous (burned at $T > 550$ °C) carbon deposits. TEM observations (Figure 3d) also confirmed the problematic presence of filamentous carbon for this sample.

The higher catalytic activity and sensibility towards carbon formation of Ni10/Al_2O_3-IMP sample can be explained by the presence of easily reduced bulk nickel oxide (NiO) evidenced during the TPR measurement (Figure 5). Indeed, during the catalytic test performed at 650 °C, bulk NiO was instantly activated at the beginning of the test. As this type of nickel oxide is known to present the highest catalytic activity but also the lowest interactions with the support, it was quickly deactivated by coking mechanisms [33, 34]. Furthermore, the sintering of NiO crystallites was increased by the fact that this type of nickel oxide shows low interactions with the alumina support. This would explain that Ni10/Al_2O_3-IMP samples presented larger $Ni^{(0)}$ particles with a broad distribution of sizes after a catalytic test compared to Ni10/Al_2O_3 sample (Table 3). The growth of filamentous carbon being more favorable in the presence of large metallic particles [36–38], this would also explain why Ni10/Al_2O_3-IMP sample presented filamentous carbon, whereas Ni10/Al_2O_3 sample only presented amorphous carbon (Figure 6b). Hence, after 105 min of test, it was assumed that all NiO crystallites were deactivated by coke and the stable C_T value of Ni10/Al_2O_3-IMP sample was only guaranteed by the nickel which strongly interacted with the support (coming from NiO/Al_2O_3 and $NiAl_2O_4$).

The stable catalytic activity and low carbon deposit observed for Ni10/Al_2O_3 sample was attributed to the initial presence of nickel oxide which strongly interacted with the support ($NiAl_2O_4$). However, at this stage, the behavior of Ni10/Al_2O_3 sample during the catalytic test was not fully understood. Indeed, being that the TPR measurement (Figure 5a) indicated that the reduction of the $NiAl_2O_4$ phase only started at 680 °C, this sample was progressively reduced into the catalytic reactor by the syngas mixture during the catalytic tests performed at 650 °C and presented $Ni^{(0)}$ nanoparticles after catalytic tests (evidenced by XRD and TEM measurements). Hence, it seemed that the composition of the syngas influences the reducibility of the catalyst (further details in section 3.3).

Moreover, as the catalytic experiments are made at 650°C and, as observed on Figure 5, the reduction of Ni species occurs at higher temperature, the degree of Ni reduction is probably different in both samples which can also influence the catalytic activity. But in both cases, Ni^0 is well observed on the post catalytic experiment analysis (Table 3) showing at least a partial reduction of the catalysts during the experiments at 650 °C.

In this way, it appears that the 10 wt.% Ni/γ-Al_2O_3 catalyst prepared by the sol-gel process, represents a compromise between catalytic efficiency and resistance to coking deactivation for the reforming of 24.000 ppmv of toluene at 650 °C. Therefore, this study confirms the advantage of the use of sol-gel instead of wet impregnation methods for this application due to better resistance to coking.

3.3. Influences of the syngas composition

Several catalytic tests were performed in order to understand why Ni10/Al_2O_3 sample was activated at 650 °C during the test performed in section 3.2 (Figure 6a) whereas it was reduced only at 680 °C during H_2-TPR measurement (Figure 5). These tests also allowed understanding the influence of the presence of methane in the syngas mixture, to estimate the fraction of toluene converted either to CH_4, or to CO and H_2, and to estimate the influence of the presence of a catalyst on the composition of the syngas mixture by parallel reactions.

The sol-gel prepared Ni10/Al_2O_3 catalyst was tested for 300 min at 650 °C according to the following conditions: i) standard conditions ; ii) without methane; iii) without toluene; iv) with standard conditions until 105 min of test, after toluene was removed from the syngas mixture; v) without methane and without toluene.

Table 1 shows the composition of the gas mixtures during the catalytic tests. When the catalytic test was performed without neither methane nor toluene (condition v), the volumic percentages of CO and H_2O decreased (ΔV_{CO} = - 2.0 %; ΔV_{H2O} = - 1.6 %) and the volumic percentages of CO_2 and H_2 increased (ΔV_{CO2} = + 2.5 %; ΔV_{H2} = + 0.7 %). This effect was mainly attributed to the Water-Gas Shift reaction ($CO+H_2O\leftrightarrow CO_2+H_2$), which can occur on Al_2O_3 supports doped with metallic oxides [39, 40].

Figures 7a and 7b show the X-Ray diffraction patterns and the DSC curves performed on sample Ni10/Al_2O_3 after catalytic tests performed in different conditions (i to v). Ni10/Al_2O_3 sample tested without methane (condition ii) presented slightly higher C_T and lower S_B values compared to the standard condition i (ΔC_T = + 4 %; ΔS_B = - 5 %). However, the absence of methane in the syngas mixture favored the formation of filamentous carbon (Figure 7b). Therefore, it was assumed that under standard test condition i, the higher covering of the metallic Ni particles by carbon species adsorbed on the surface (C_α^* species), coming from methane, decreased the adsorption and ring-breaking of the toluene molecules, which would explain the lower C_T and S_B values. However, the high covering of the metallic particles by carbon species, coming from methane, might prevent the condensation of large polymeric carbons by the “ensemble control” effect between C_α^* and graphitic carbon (C_β^*) species, which could explain the absence of filamentous carbon for Ni10/Al_2O_3 sample.

When no methane was added to the syngas mixture (conditions ii and v), no methanation reactions ($CO+3.H_2 \leftrightarrow CH_4+H_2O$ or $2.CO+2.H_2 \leftrightarrow CH_4+CO_2$) occurred during the test in condition v (Table 1), but in condition ii, there was a slightly production of methane (+ 0.7 vol. %) during the catalytic test. Hence, it was deduced that this amount of methane was entirely generated from the conversion of toluene molecules. According to Equation 6, the fraction of toluene converted to methane (Y_{CH4}) was estimated to be about 9 %. Since this value was very close to the S_{B} value (10 %) (Table 1), it was assumed that methane was produced by hydrodealkylation ($toluene+H_2 \rightarrow benzene+methane$).

Interestingly, for in both conditions iv and v, on the X-Ray patterns after catalytic tests at 650 °C (Figures 7a), no characteristic $\mathrm{Ni}^{(0)}$ peaks, but only NiO peaks, were observed. However, the small intensity of the NiO peaks suggested that a part of nickel atoms might also be incorporated into the γ-Al_2O_3 support in a $NiAl_2O_4$ spinel (not visible by XRD because of the presence of γ-Al_2O_3 peaks at the same diffraction angles). The absence of $\mathrm{Ni}^{(0)}$ particles for both samples was also confirmed by TEM measurements (not shown).

Analysis of the X-Ray pattern for sample tested in condition iii (Figure 7a) revealed similar trends. Indeed, whereas the X-Ray pattern of sample tested in condition i presented only $\mathrm{Ni}^{(0)}$ peaks after the catalytic test (Figure 7a), the sample tested in condition iii presented very small peaks of $\mathrm{Ni}^{(0)}$ and more larger characteristic peaks of NiO (Figure 7a). Hence, it appeared that the removal of the toluene from the syngas mixture at 105 min during the catalytic test led to a re-oxidization of the $\mathrm{Ni}^{(0)}$ particles of $Ni10/Al_2O_3$ sample by H_2O and CO_2. These observations can be correlated with the works of Cheng *et al.* [41, 42]. Indeed, it was found that, at temperatures above 450 °C, the reduction of NiO/α-Al_2O_3 catalysts was thermodynamically more favorable with several organic compounds (glucose, furfural, acetic acid, ethanol and acetone) than with common reducing agent (CO, H_2). Figure 8 shows the mechanism of reduction proposed by Cheng et *al.* [41, 42] adapted to this case with toluene. It was decided in the present work to call this phenomenon “special reduction by toluene”. In a first step, the toluene is adsorbed on NiO and on the alumina support. Thereafter, the toluene molecules are decomposed into carbon (char). NiO and the char react to form $Ni^{(0)}$ and CO_2. Then CO_2 reacts with the char located at the surface of the support to form CO, which can further reduce the remaining nickel oxides into $Ni^{(0)}$.

Table 4 shows the Gibb’s free energy values calculated for the reduction of bulk NiO with different compounds. The values presented are only informative since they were calculated for the reduction of bulk NiO, which is very different from the case of nickel oxide nanoparticles highly dispersed on γ-Al_2O_3. When CO and H_2 are used as reducing agents (Table 4), the exothermic aspect ($\Delta H_{923K} < 0$) of the “$NiO+H_2$” and “$NiO+CO$” reactions is the main driving force. In the opposite, when C, CH_4 or toluene are used as reducing agents, the reactions of NiO reduction are endothermic ($\Delta H_{923K} > 0$). Hence, for C, CH_4 and toluene, negative ΔG_{923K} values are obtained by an increase of the entropy caused by the production of more gas volumes [41, 42].

Either considering the formation of CO and H_2 (Equation 8), or the formation of CO_2 and H_2O (Equation 9) (Table 4), the reduction of NiO is thermodynamically more favorable with toluene than with methane or with standard reducing agents (CO, H_2). Furthermore, toluene being more inclined to form carbon deposit than methane, this would increase the reduction of NiO into $Ni^{(0)}$ by formation of char according to the reduction mechanism proposed in Figure 8. Finally, this phenomenon is emphasized by the fact that the $Ni^{(0)}$ nuclei, formed during the reduction of NiO, increase the adsorption-dissociation of H_2 by the “spillover effect” [43, 44] and consequently greatly increase the rate of reduction [45]. Hence, once the reduction is initiated by toluene, and that metallic $Ni^{(0)}$ is present, the reduction can occur with other reductive molecules (CO and H_2) and leads to the whole reduction of the catalyst. This would explain why Ni10/Al_2O_3 sample tested in condition i only presented characteristic peaks of $Ni^{(0)}$ on its X-Ray patterns (Figure 7a).

During the catalytic test, the atmosphere is reductive ($P_{CO}/P_{CO2} = 2.1$ and $P_{H2}/P_{H2O} = 2.9$). However, in this case, Ni and γ-Al_2O_3 showed very strong interactions: exclusive presence of $NiAl_2O_4$ spinel and starting of the reduction only at 680 °C under standard H_2-TPR (Figure 5). Furthermore, during the catalytic tests performed at 650 °C, Ni10/Al_2O_3 sample was tested below its initial theoretical temperature of reduction. So, this would explain the removal of toluene during the catalytic test at 105 min led to a re-oxidization of the $Ni^{(0)}$ particles for sample of condition iii (see XRD, Figure 7a).

The low formation of carbon and the good resistance against deactivation by coking observed for Ni10/Al_2O_3 sample tested in condition i were attributed to the fact that the catalytic tests were performed at the boundary between the oxidation and the reduction of Ni nanoparticles. In this way, it was assumed that during a standard catalytic test (condition i), as soon as some areas of the $Ni^{(0)}$ particles were re-oxidized by CO_2 or H_2O, they would be quickly reduced again by the phenomenon of "special reduction by toluene" (Equations 8 and 9, Table 4). Hence, this effect would reduce the formation of carbon deposit.

This hypothesis could explain why, in section.3.2, the presence of initial bulk NiO caused a severe deactivation of Ni10/Al_2O_3-IMP sample during the catalytic test performed at 650 °C, while Ni10/Al_2O_3 sample presented a stable activity. Indeed, since the bulk NiO present in Ni10/Al_2O_3-IMP sample was reduced at low temperature ($T \sim 450$ °C), it was not able to take advantage of the anti-coking properties provided by the phenomenon of "special reduction by toluene".

3.4. Influences of the nickel loading

3.4.1. Physico-chemical properties of Ni10/γ-Al_2O_3 catalysts with different loadings

The influences of the nickel loading on properties and catalytic performances of Ni/γ-Al_2O_3 catalysts were studied for Ni loadings equal to 10, 20, 30 and 50 wt.%. TEM measurements (Figures 3a and 3c) revealed that all samples presented homogenous structure at nanoscopic scale. It was also observed by XRD measurements (not shown here) that all samples presented γ-Al_2O_3 phases.

Figure 9 presents the nitrogen adsorption-desorption isotherms and the associated pore size distribution of all samples. The textural values (S_{BET}, V_p and V_{DR}) of the samples are listed in Table 2. It was observed that all samples presented a hysteresis, characteristic of mesoporous samples (Figure 9a). Furthermore, all samples were also highly microporous. Indeed, V_{DR} values were equal of about 0.08 cm^3/g, except for Ni50/Al_2O_3 sample, for which V_{DR} was slightly lower (0.05 cm^3/g). In that case, the high amount of nickel added clogged a part of micropores and small mesopores. Finally, the nickel loading did not affect the mesopore size distributions of the samples (Figure 9b).

Figure 10 shows the TPR profiles of pure nickel oxide (NiO) and of Ni/γ-Al_2O_3 catalysts with different nickel loadings. For all samples, the reduction was almost complete (between 90 and 100 %) when the temperature reached 1000 °C. Whereas Ni10/Al_2O_3 sample presented only one peak of nickel aluminate ($NiAl_2O_4$), higher loadings of Ni led to the presence of other nickel/alumina oxides. In this way, in addition to a $NiAl_2O_4$ peak, Ni20/Al_2O_3 sample also presented a small peak of bulk nickel oxide (NiO) located at 475 °C. Furthermore, a notable shift of the $NiAl_2O_4$ peak ($\Delta T = -75$ °C) was observed for this sample. This important shift was attributed to the presence of easily reduced bulk nickel oxide (NiO). NiO being converted to metallic nickel at low temperature, it can favor the adsorption-dissociation of H_2 molecules by "spillover effect" [43, 44] and improve the reduction of more stable oxide phases like NiO/Al_2O_3 or $NiAl_2O_4$.[29, 32, 43]. Higher loadings of Ni (Ni30/Al_2O_3 and Ni50/Al_2O_3

samples) led to more intense peaks of bulk nickel (NiO) and to the presence of octahedral nickel (NiO/Al_2O_3), associated to a reduction peak shift of $NiAl_2O_4$ of about $\Delta T \sim -100$ °C.

It was observed in Table 2 that after the H_2 reduction step, d_{TEM}, d_{XRD} and σ_{TEM} values were relatively similar and remained low for all samples. Indeed, even for $Ni50/Al_2O_3$ sample, which presented the highest Ni loading, σ_{TEM} was only equal to 7 nm, and d_{TEM} and d_{XRD} values were only equal of about 16 nm. In this way, even for high loadings of Ni, the samples presented particles of relatively low sizes. In the opposite, after TPR measurements, the standard deviation values became very important for $Ni30/Al_2O_3$ and $Ni50/Al_2O_3$ samples ($\sigma_{TEM} = 28$ nm and $\sigma_{TEM} = 64$ nm respectively) (Table 2) and very large nickel particles (up to 200 nm) were observed by TEM measurements. It was also observed that as the nickel content increased, the differences between d_{TEM} and d_{XRD} values became more and more important ($Ni50/Al_2O_3$ sample showed the highest difference: $d_{TEM} = 50$ nm and $d_{XRD} = 28$ nm). These strong differences can be explained by the fact that, during TPR measurements, the Ni particles submitted important sintering being that the temperature was increased until 1000 °C, and formed large agglomerates constituted of crystallites with different diffraction plans. In addition to the high content of metal, it was assumed that the high sensibility of $Ni30/Al_2O_3$ and $Ni50/Al_2O_3$ samples towards sintering was also provoked by their high amount of bulk nickel (NiO), which is known to easily sinter because of its low interactions with the support.[29, 33, 34]

3.4.2. Catalytic activity of $Ni/\gamma\text{-}Al_2O_3$ catalysts with different Ni loadings

The catalytic activity of all samples were evaluated for the reforming of 24.000 ppmv of toluene for 5 h at 650 °C. The toluene conversion values as a function of time are presented in Figure 11a. Table 5 shows the metallic nickel particles sizes after catalytic tests, and the catalytic performances of all samples. Figure 11b shows the DSC curves of samples after catalytic tests. As for the comparison between impregnated and sol-gel samples, the degree of

Ni reduction is probably different in the samples and can also influence the catalytic activity. But in all cases, Ni^0 is well observed on the post catalytic experiment analysis (Table 5) showing at least a partial reduction of the catalysts during the experiments at 650 °C.

In Figure 11a, whereas the toluene conversion for Ni10/Al_2O_3 sample remained stable around 50 % throughout the catalytic test, Ni20/Al_2O_3 sample showed a drastic loss of toluene conversion during the first 100 min of test (ΔC_T ~ - 35 %). Nevertheless, around 150 min of test, the conversion of toluene stabilized (C_T ~ 62 %). Despite its higher toluene conversion, compared to Ni10/Al_2O_3 sample, Ni20/Al_2O_3 sample showed a lower toluene reforming rate ($r_T = 0.047$ $mol_{Tolu}/(g_{Ni}.h)$ *vs.* $r_T = 0.067$ $mol_{Tolu}/(g_{Ni}.h)$) and a much higher trend to form carbon deposit ($Coke^* = 0.16$ g_{Carbon}/g_{Tolu}, *vs.* $Coke^* = 0.031$ g_{Carbon}/g_{Tolu}) (Table 5). Furthermore, Ni20/Al_2O_3 sample presented a large amount of carbon deposit after test ($Coke = 0.71$ g_{Carbon}/g_{Cata}) which was either amorphous (burned at $T < 550$ °C) and filamentous (burned at $T > 550$ °C) (Figure 11b). The presence of a high amount of filamentous carbon for Ni20/Al_2O_3 sample was confirmed by TEM measurements (as in Figure 3d). Similarly to Ni10/Al_2O_3-IMP sample presented in section 3.2, the deactivation by coking of Ni20/Al_2O_3 sample was attributed to the presence of bulk nickel (NiO). As this type of nickel oxide is easily reducible (T ~ 450 °C), it was quickly activated at the beginning of the catalytic test, which explains the high initial C_T value (nearly equal 100 %) showed by Ni20/Al_2O_3 sample. However, since NiO was reduced at low temperature, it could not take advantage of the anti-coking influence caused by the mechanism of "special reduction by toluene" described in section 3.3. This explains why Ni20/Al_2O_3 sample was quickly deactivated during the test. Hence, it was assumed that, during the catalytic test of Ni20/Al_2O_3 sample presented in Figure 11a, around 150 min, NiO was totally deactivated and the stable C_T observed for the rest of the test was only guaranteed by $Ni^{(0)}$ nanoparticles with strong interactions with the alumina support.

The fact that the toluene conversion of Ni30/Al_2O_3 sample was nearly equal to 100 % during the catalytic test (Figure 11a) must be interpreted with caution. Indeed, during the test, the pressure drop increased until reaching a stable value of 0.3 bar around 60 min, which was sustainable for the experimental installation, but could be problematic at higher scale. Ni30/Al_2O_3 sample presented a very high amount of carbon deposit ($Coke$ = 1.21 g_{Carbon}/g_{Cata}), which was mostly composed of filamentous carbon (Figure 3d, Table 5 and Figure 11b). This sample did not produce benzene (S_B = 0 %). In view of these observations, it was assumed that the high tendency of Ni30/Al_2O_3 sample to form filamentous carbon was also caused by the presence of bulk NiO. The total conversion of toluene during the test was explained by the presence of a large amount of nickel, which would compensate the deactivation of one fraction of it during the test. The almost total conversion of toluene could also be partially due to the high coking of the sample, which would consume toluene and benzene to form carbon deposit.

Ni50/Al_2O_3 sample also presented a complete conversion of toluene, but the test had to be stopped after 15 min because of a too high pressure drop (1 bar). TEM and DSC measurements (not shown here) performed after test revealed that the clogging of the reactor was also provoked by a considerable formation of filamentous carbon, which was assumed to be caused by the initial presence of bulk nickel NiO in large amounts (Figure 10).

In Table 5, it is observed that the three catalysts Ni10/Al_2O_3, Ni20/Al_2O_3 and Ni30/Al_2O_3 did not submit excessive sintering for Ni nanoparticles during the catalytic test. The size of the Ni particles being also a crucial factor for the formation of filamentous carbon, this observation confirmed the fact that the sensibility of the Ni/γ-Al_2O_3 catalysts against coking mechanisms was strongly influenced by the initial presence of nickel with low interactions with the support (NiO), and not by the size of Ni particles present in the different catalysts.

From all these results, it appeared essential to prevent the formation of bulk NiO for two reasons: i) its low interactions with the γ-Al_2O_3 support favoring the formation of filamentous carbon; ii) by showing a reduction temperature (450 °C) lower than the temperature of catalytic test (650 °C), NiO cannot take advantage of the anti-coking phenomenon of "special reduction by toluene".

In this way, despite the fact that the sol-gel procedure permits to prepare very micro- and mesoporous Ni/γ-Al_2O_3 catalysts, even at high doping of metals (up to 50 wt.%), it appeared that the 10 wt.% Ni/γ-Al_2O_3 catalyst was the best compromise between catalytic activity and coking resistance for the reforming of 24.000 ppmv of toluene at 650 °C. Indeed, because of the exclusive presence of a $NiAl_2O_4$ phase, Ni10/Al_2O_3 sample was able to beneficiate from the mechanism of "special reduction by toluene" which allowed protecting the catalyst from deactivation by coking.

4. Conclusions

In this work, Ni/γ-Al_2O_3 catalysts were prepared by a new aqueous sol-gel method with different Ni loadings (10, 20, 30 and 50 wt.%) and were compared for the reforming of toluene at 650 °C. A sample was also prepared by wet impregnation with 10 wt.% of Ni and compared to the corresponding sol-gel sample. So this study was divided in three main parts: (i) the comparison of a catalyst with 10 wt.% of Ni prepared by sol-gel process and impregnation, (ii) the influence of the gas composition on the catalytic performance of the sol-gel Ni/γ-Al_2O_3 catalyst with 10 wt.% of Ni and (iii) the influence of Ni loading on the catalytic activity.

When 10 wt.% Ni/γ-Al_2O_3 catalysts prepared by sol-gel process or wet impregnation method were compared, it was observed that, whereas the sample prepared by the sol-gel method presented only a $NiAl_2O_4$ spinel phase, the catalyst prepared by wet impregnation showed different nickel oxide species (bulk NiO, NiO/Al_2O_3 and $NiAl_2O_4$). Tested for the reforming of toluene at 650 °C, the catalyst prepared by wet impregnation showed a high initial toluene conversion followed by an important deactivation. This behavior confirmed the fact that the presence of bulk NiO, which shows low interactions with the alumina support and which is reduced at lower temperatures (around 450 °C) than the catalytic tests, should be avoided.

The stable catalytic activity and relatively low carbon deposit observed for 10 wt. % Ni/γ-Al_2O_3 catalyst prepared by the sol-gel process was explained by the fact that, during catalytic test performed at 650 °C, the sample was tested at the boundary between the reduction and oxidation of Ni nanoparticles. The calculation of the Gibb's free energy values at this temperature showed that, from a thermodynamic point of view, the toluene is a more effective reducing agent compared to CO or H_2. Indeed, without toluene in the syngas mixture, the catalyst did not show $Ni^{(0)}$ particles after catalytic test, but NiO particles. Furthermore, it was observed that, if toluene was withdrawn from the syngas mixture during the catalytic test, the sample was progressively re-oxidized by CO_2 and H_2O.

As the Ni loading increased (from 10 wt. % to 50 wt. %), $NiAl_2O_4$ was progressively joined by nickel oxide with low interactions (NiO/Al_2O_3) and bulk nickel oxide (NiO). This led to a high initial conversion of toluene, but also to a progressive loss of the catalytic activity throughout the catalytic test. In addition to low metal/support interactions, the high sensibility of NiO towards coking was also attributed to the fact that NiO was reduced at a lower temperature (~ 450 °C) than the catalytic test (650 °C), and hence did not take advantage of the anti-coking effect brought by the phenomenon of "special reduction by toluene". It was shown that the sol-gel method developed throughout this work allowed synthesizing very porous and highly dispersed Ni/γ-Al_2O_3 catalysts with high amounts of Ni.

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Compliance with ethical standards

Conflict of interest: The authors declare that they have no conflicts of interest.

Data availability

The raw/processed data required to reproduce these findings cannot be shared at this time as the data also forms part of an ongoing study.

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Table 1: Evolution of the gas composition and catalytic performances of Ni10/Al_2O_3 sample tested under different atmospheres.

Sample condition		Gas composition (vol. %)					Catalytic performances	
		CO_2	H_2O	H_2	CH_4	CO		
Condition i	Blank	16.2	12.8	29.0	11.2	30.8	C_T = 51 %	**Coke** = 0.10 g_{Carbon}/g_{Cata}
	Test	15.8	7.3	33.1	10.2	33.6	C_{CH4} = 10 %	S_B = 15 %
	ΔV	- 0.4	- 5.5	+ 4.1	- 1.0	+ 2.8		
Condition ii	Blank	15.7	14.0	30.0	0.0	31.0	C_T = 54 %	**Coke** = 0.11 g_{Carbon}/g_{Cata}
	Test	15.5	7.0	34.0	0.7	34.3	C_{CH4} = #	S_B (%) = 10 %
	ΔV	- 0.2	- 7.0	+ 4.0	+ 0.7	+ 3.3		
Condition iii	Blank	17.6	13.4	29.6	8.0	31.4	C_T = #	**Coke** = 0.04 g_{Carbon}/g_{Cata}
	Test	18.9	9.9	33.7	6.0	31.5	C_{CH4} = 25 %	S_B = #
	ΔV	+ 1.3	- 3.5	+ 4.1	- 2.0	+ 0.1		
Condition iv	Blank	16.9	12.4	29.7	9.4	31.6	C_T = #	**Coke** = 0.02 g_{Carbon}/g_{Cata}
	Test	18.3	10.7	30.8	9.1	31.1	C_{CH4} = 3 %	S_B = #
	ΔV	+ 1.4	- 1.7	+ 1.1	- 0.3	- 0.5		
Condition v	Blank	16.2	12.6	30.0	0.0	32.2	C_T = #	**Coke** < 0.01 g_{Carbon}/g_{Cata}
	Test	18.7	11.0	30.7	< 0.1	30.2	C_{CH4} = 0	S_B = #
	ΔV	+ 2.5	- 1.6	+ 0.7	0.0	- 2.0		

Test conditions: 650 °C, 300 min, 24.000 ppmv of toluene, *GHSV* of 5000 h^{-1}; The evolutions of the volume percentages (*ΔV*) were established by comparing the average of the blank measurements before the test and the average of the 10 last values during the test.

C_T: conversion of toluene; S_B: selectivity in benzene; C_{CH4}: conversion of methane; *Coke*: carbon deposit amount after 5 h of test measured by TG-DSC; #: No value expected.

Table 2: Theoretical, actual compositions and physico-chemical properties of Ni/γ-Al_2O_3 catalysts.

Sample	Al_2O_3 content		Ni content		S_{BET} (m^2/g)	V_p (cm^3/g)	V_{DR} (cm^3/g)	Ni particle size			
								Post-H_2 Reduction		Post-TPR	
	Theo. (wt. %)	Exp. (wt. %)	Theo. (wt. %)	Exp. (wt. %)				d_{TEM} (nm)	d_{XRD} (nm)	d_{TEM} (nm)	d_{XRD} (nm)
Ni10/Al_2O_3	90.0	89.5	10.0	10.5	240	0.3	0.08	8 ± 2	9	30 ± 9	23
Ni20/Al_2O_3	80.0	79.7	20.0	20.3	225	0.3	0.08	9 ± 3	10	39 ± 12	25
Ni30/Al_2O_3	70.0	68.6	30.0	31.4	200	0.3	0.07	12 ± 5	12	45 ± 28	27
Ni50/Al_2O_3	50.0	51.2	50.0	48.2	135	0.2	0.05	17 ± 7	15	50 ± 64	28
Ni10/Al_2O_3-IMP	90.0	91.1	10.0	8.9	210	0.2	0.08	10 ± 3	10	35 ± 15	24

S_{BET}: specific surface area; V_p: porous volume; V_{DR}: microporous volume; d_{TEM}: metallic particles size median measured by TEM; d_{XRD}: metallic nickel crystallites size obtained by XRD.

Table 3: Ni particles size and catalytic performances of samples prepared by sol-gel or by impregnation methods.

Sample	Ni particles size after catalytic test		Catalytic performances						
	d_{TEM} (nm)	d_{XRD} (nm)	C_T (%)	r_T ($mol_{Tolu}/(g_{Ni}.h)$)	C_{CH4} (%)	S_B (%)	*Coke* (g_{Carbon}/g_{Cata})	*Coke** (g_{Carbon}/g_{Tolu})	*Fil. carbon*
Ni10/Al_2O_3	11 ± 3	12	51	$6.7 .10^{-2}$	10	15	0.10	$3.1 .10^{-2}$	+
Ni10/Al_2O_3-IMP	15 ± 7	14	50	$7.6 .10^{-2}$	13	8	0.28	$8.9 .10^{-2}$	++

Test conditions: 650 °C, 300 min, 24.000 ppmv of toluene, *GHSV* of 5000 h^{-1}.

d_{TEM}: particle size median measured by TEM; d_{XRD}: crystallites size estimation obtained by XRD; C_T: conversion of toluene; r_T: reaction rate of toluene reforming; S_B: selectivity in benzene; C_{CH4}: conversion of methane; *Coke*: carbon deposit amount after 5 h of test measured by TG-DSC; *Coke**: tendency of sample to form carbon deposit; Fil. carbon: filamenteous carbon.

Table 4: Variation of Gibb’s free energy, enthalpy and entropy values for the reduction of bulk NiO with either toluene, CH_4, H_2, CO or C as reducing agent.

Equations of reduction	ΔH_{923K} (kJ/mol$_{NiO}$)	ΔS_{923K} (kJ/(mol$_{NiO}$.K))	ΔG_{923K} (kJ/mol$_{NiO}$)	Eq. n°
$C_7H_8 + 7\ NiO \rightarrow 7\ Ni + 7\ CO + 4\ H_2$	140	0.252	-93	(8)
$C_7H_8 + 18\ NiO \rightarrow 18\ Ni + 7\ CO_2 + 4\ H_2O$	38	0.105	-59	(9)
$CH_4 + NiO \rightarrow Ni + 2\ H_2 + CO$	215	0.331	-90	(10)
$CH_4 + 4\ NiO \rightarrow 4\ Ni + 2\ H_2O + CO_2$	45	0.100	-47	(11)
$H_2 + NiO \rightarrow Ni + H_2O$	-6	0.038	-41	(12)
$CO + NiO \rightarrow Ni + CO_2$	-48	0.003	-51	(13)
$C + NiO \rightarrow Ni + CO$	138	0.202	-48	(14)
$C + 2\ NiO \rightarrow 2\ Ni + CO_2$	45	0.095	-43	(15)

ΔH_{923K} : enthalpy change at 650 °C ; ΔS_{923K}: entropy change at 650 °C; ΔG_{923K}: Gibb’s free energy change at 650 °C. The enthalpy and entropy values were determined from the references values obtained in the website of National Institute of Standards and Technology and by applying the following equations: $\Delta H_{923K} = \Delta H^0_{298K} + C_p * (923 - 298)$ and $\Delta S_{923K} = \Delta S^0_{298K} + C_p * ln(923/298)$.

These values are calculated at 650 °C per mol of NiO reduced.

Table 5: Ni particles sizes and catalytic performances of Ni/γ-Al_2O_3 catalysts with different nickel loadings.

Sample	**Ni particles size**		**Catalytic performances**						
	d_{TEM} (nm)	d_{XRD} (nm)	C_T (%)	r_T ($mol_{Tolu}/(g_{Ni}.h)$)	C_{CH4} (%)	S_B (%)	*Coke* (g_{Carbon}/g_{Cata})	*Coke** (g_{Carbon}/g_{Tolu})	*Fil. carbon*
Ni10/Al_2O_3	11 ± 3	12	51	0.067	10	15	0.10	0.031	No
Ni20/Al_2O_3	12 ± 8	12	62	0.047	7	5	0.71	0.16	++
Ni30/Al_2O_3[a]	18 ± 13	14	99	0.290	9	0	1.21	0.20	+++
Ni50/Al_2O_3	The test was stopped at *t* = 15 min because of too high pressure drop (*P* = 1 bar).								

Test conditions: 650 °C, 300 min, 24.000 ppmv of toluene, *GHSV* of 5000 h^{-1}.

d_{TEM}: metallic particles size median measured by TEM; d_{XRD}: metallic crystallites size estimation obtained by XRD. C_T: conversion of toluene, r_T: reaction rate of toluene, S_B: benzene selectivity, C_{CH4}: methane conversion. *Coke*: carbon deposit amount after 5 h of test measured by TG-DSC, *Coke**: tendency of sample to form carbon deposit; Fil. carbon: filamenteous carbon.

[a] The pressure drop increased during the test and reached a stable value of P = 0.3 bar at t = 60 min.