# Ni- and Fe-doped $\gamma$-$Al_2O_3$ or Olivine as primary catalyst for toluene reforming

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## Abstract

In this paper, $\gamma$-$Al_2O_3$ supports prepared by a new aqueous sol-gel synthesis were doped with 2 wt. % of Ni or 10 wt. % of Fe and used as primary catalysts for the bio-syngas purification. Raw olivine, Ni- and Fe-doped olivine catalysts were also prepared for comparison with alumina-based samples. The physico-chemical properties of the samples were characterized by X-ray diffraction, nitrogen adsorption-desorption and temperature programmed reduction. Results showed that alumina-based samples were more porous than olivine-based ones. Stronger interactions of the dopants with the support were highlighted in the case of alumina samples. The catalysts were then tested at two temperatures, 750 and 850

°C, for the toluene reforming. Toluene was chosen as biomass gasification tar model molecule. At 750 °C, the Ni/olivine sample showed a higher toluene conversion and a lower benzene selectivity than the Ni/alumina sample. This lower catalytic activity was attributed to strong interactions between nickel and alumina (formation of a spinel $NiAl_2O_4$). At 850 °C, similar performances were obtained both for olivine and for alumina supports. However, due to lower interactions with the support and a better reduction of Ni, the methane conversion of the Ni/olivine sample was higher than that of the Ni/alumina sample.

## 1. Introduction

Adapted from old coal gasification technologies developed during the industrial revolution, the biomass gasification appears nowadays as an interesting and versatile way to take advantage of different 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 high valuable chemical compounds such as methanol [1,2]. Bio-syngas is predicted to be an economically viable energy and some industrial plants are already in operation. However bio-syngas technologies still encounter some technical problems, which seriously hinder their commercial development [3,4]. One major problem is the presence of tar at the gasifier outlet. This tar results from the incomplete degradation of aromatic rings contained in the biomass. Modifications of the design and the operating conditions (temperature, space ratio, gasifying reagent) of the gasifier have proved to substantially reduce the tar concentration [5–9]. Furthermore, the catalytic reforming of tars inside or outside the gasifier also appears to be a convenient and economical solution to obtain a clean bio-syngas, explaining the numerous studies published the last two decades on this topic [3,9–15]. Intensive research has been undertaken regarding various aspects of the catalysts

formulation, such as the type of catalysts, the acido-basicity, the texture, the crystallinity or the elementary composition of the supports and active sites. Furthermore, the lifetime and performances of the catalysts are strongly dependent to the operating conditions such as the temperature, space ratio or gas mixture.

The catalysts for the bio-syngas purification can be used either directly inside (primary catalysts – fluidized bed reactor) or at the outlet (secondary catalysts - fixed bed reactor) of the biomass gasifiers. Depending on their location, the catalysts do not operate under the same conditions and do not require the same properties. In the case of primary catalysts, stability at high temperatures (750-900 °C) is required [14,15].

Different catalyst supports can be used as $Al_2O_3$ [16–18], olivine [11–13] or carbon-based materials [19–21]. With its non-toxicity, low cost and high attrition resistance, olivine mineral ($(Mg,Fe)_2SiO_4$) has proved to be a valuable support for primary catalysts. Doped either with Ni [11–13] or Fe [22–24], this natural mineral presents very interesting catalytic performances for the reforming of tars. According to literature, $\gamma$-$Al_2O_3$ is also a promising support for reforming applications [25–27] thanks to (i) a large specific surface area (200-500 $m^2/g$), (ii) a high mechanical strength and (iii) a good sintering resistance. Though $\gamma$-$Al_2O_3$ is one of the most common catalytic support, no direct comparison between $\gamma$-$Al_2O_3$ and olivine materials doped with metallic elements and tested in primary conditions has been noticed yet.

From a catalytic and economic point of view, nickel is known to be the most interesting metallic dopant for reforming applications [3,9,10]. Its loading usually varies from 1 to 20 wt. %. However, at high temperatures (> 800 °C), it is generally recommended to use small amounts of doping (< 5 wt. % Ni) in order to promote interactions with the support, to keep small metallic nanoparticles and to prevent deactivation by sintering [9,28]. Despite a high efficiency, nickel-doped materials can be problematic in primary conditions because of the formation of toxic nickel dusts due to catalyst attrition in the case of a fluidized bed. Hot filters are therefore

required in order to get rid of these toxic dusts. For these reasons, some studies have focused on the development of iron-based materials for primary catalyst applications. Despite lower catalytic performances, iron oxides and especially metallic iron supported on various supports ($Al_2O_3$, olivine, scallop shell…) have proved to be interesting for the reforming of gasification tars. However, the low activity of the iron species requires high amounts of dopant, generally between 10 and 30 wt. % [14,15,22]. The catalytic activity of the iron species generally increases with their reduction states ($Fe_2O_3 < Fe_3O_4 < FeO < Fe^{(0)}$)[29–32]. The experiments must therefore be performed at a sufficiently high temperature in order to favor a partial or complete reduction of the iron species (> 750 °C).

In this work, $\gamma$-$Al_2O_3$ supports, prepared by a newly developed aqueous sol-gel process, were doped with either 2 wt. % of Ni or 10 wt. % of Fe for the bio-syngas purification and used as primary catalysts. In order to compare the performances of the $\gamma$-$Al_2O_3$ based samples with commonly used catalysts, olivine catalysts doped with either Ni or Fe were also prepared by an impregnation method [11,22]. Olivine-based and alumina-based catalysts were compared regarding their physico-chemical properties (as texture, composition or crystallinity), their method of preparation and also their catalytic activity on tar reforming. To our best knowledge, this comparison is not reported in literature. Toluene was used as biomass gasification tar model molecule [20,21]. The catalysts were tested on the reforming of toluene in primary conditions (750 °C or 850 °C). Their catalytic performances, which include their catalytic activities (toluene conversion, methane conversion and benzene selectivity) and their stability against deactivation mechanisms (coking, sintering and phase change), were evaluated and compared. The interactions between the dopants and the support were highlighted through the characterizations.

## 2. Materials and Methods

## 2.1. Catalyst preparation

The samples are denoted XY/$Al_2O_3$ or XY/Olivine for catalysts supported on $\gamma$-$Al_2O_3$ and olivine respectively. The prefixes "XY" are related to the nature X (Ni or Fe) and the concentration Y (2 wt. % of nickel or 10 wt. % of iron) of dopant. For example, Ni2/$Al_2O_3$ denotes a catalyst with 2 wt. % of nickel supported on alumina.

### 2.1.1. Sol-Gel synthesis of Ni- and Fe/$\gamma$-$Al_2O_3$ catalysts

Three alumina-based catalysts were synthesized according to a procedure adapted from [33]. First, aluminum precursor (aluminum nitrate, $Al(NO_3)_3.9H_2O$, ≥ 98%, Sigma Aldrich) was dissolved in with water. Then, the sols were formed by slow addition of a $NH_4OH$ solution (30 wt. %, 15 M). After precipitation, the sols were stirred for 24 h at 85 °C, washed two times with water, re-dispersed in water and doped with the corresponding metallic salts. The adequate amount of either nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$, 99.99%, Sigma Aldrich) or iron nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$, ≥ 99.95%, Sigma Aldrich) was added to obtain either 2 wt. % of Ni or 10 wt. % of Fe doped alumina. After 30 min of stirring, the bottles were opened and placed in an oven for aging (24 h, 85 °C, 700 mbar). Thereafter, the gels were washed twice: once with water in order to remove the residual nitrate ions from the metal doping; and once with ethanol in order to maintain a high mesoporosity during the drying step [34,35]. Finally, the gels were dried (24 h, 110 °C, 900 mbar) and calcined under air (5 h, 550 °C, 2 °C/min). The scheme of the synthesis is presented in Figure 1.

### 2.1.2. Preparation of Ni and Fe impregnated olivine

The olivine doping was performed according to the procedure established by Dariusz Swierczynski *et al.* [11] and Virginie *et al.* [22]. The olivine support was produced by Magnolithe GmbH (Austria), which improved its mechanical resistance by a calcination of 4 h at 1600 °C. The final mineral olivine is a silicate, in which magnesium and iron cations are embedded in the silicate tetrahedral structure ($(Mg_xFe_{1-x})_2SiO_4$) or present as $MgSiO_3$, $Fe_2O_3$ and spinel cubic phase ($\gamma$-$Fe_2O_3$, $Fe_3O_4$, or $MgFe_2O_4$ magnesioferrite) [22,36]. The olivine was doped with Ni or Fe by wet-impregnation. Firstly, olivine (300-700 µm) was mixed with an aqueous solution of either nickel nitrate hexahydrate ($Ni(NO_3)_2.6H_2O$, 99.99%, Sigma Aldrich) or iron nitrate nonahydrate ($Fe(NO_3)_3.9H_2O$, ≥ 99.95%, Sigma Aldrich). The solvent was then evaporated using a Rotavap device (24 h, 85 °C, 300 mbar). The sample was finally dried (24 h, 110 °C, 900 mbar) and calcined. The calcination conditions depended on the nature of the dopant. The Ni-doped olivine was calcined for 5 h at 550 °C with a heating rate of 2 °C/min. Nickel-olivine materials are generally calcined at high temperature to prevent the samples from deactivation by coking, when the catalytic tests are performed at low temperatures (< 650 °C) [11]. This is not the case in this current study. Due to the small amount of doping (2 wt. % Ni), a lower temperature was chosen to prevent the formation of stable and less active Ni-MgO species [37–39]. The Fe-doped olivine was calcined for 4 h at 1000 °C with a heating rate of 2 °C/min. According to Virginie *et al.* [22], calcination of iron-doped olivine at this temperature allows obtaining more available iron from the olivine structure and preventing the sintering of surface iron oxides by the formation of stable $MgFe_2O_4$ species.

### 2.2.Catalyst characterizations

The composition of the samples were determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES), equipped with an ICAP 6500 THERMO Scientific device.

Solid samples were crushed and then dissolved with lithium tetraborate before analysis. Aluminum, nickel, iron, silicon and magnesium loadings were obtained by comparison with standard solutions in the same medium.

The textural properties were determined thanks to nitrogen adsorption-desorption isotherms, 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, $V_{DR}$, was calculated by the Dubinin-Raduskevitch method for relative pressures $p/p_0$ lower than 0.4. The pore size distribution was determined by the Broekhoff-de Boer method (BdB) applied to the adsorption part of the nitrogen isotherm [40].

The crystallographic properties of the samples were determined by X-ray diffraction on a diffractometer Siemens D5000 (Cu-$K_\alpha$ radiation) between 30° and 80° ($2\theta$) with a step time of 18 s and a step size of 0.04 °. The sizes of metallic particles (Ni, Fe or Ni-Fe alloys) were calculated by the Scherrer equation centered on the ray (2 0 0) ($2\theta$ = 51.8°) for Ni, on the ray (1 1 0) ($2\theta$ = 44.8°) for Fe and on the ray (1 1 0) for Ni-Fe alloy ($2\theta$ = 65.0°) [41].

The sizes of metallic particles and their distribution were measured by transmission electron microscopy (TEM) performed on a CM10-PW6020 Philips Electron Microscope over approximately 100 particles. First, crushed samples were dispersed in absolute ethanol. Then a drop of the dispersion was 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 He at room temperature (15 min, 50 mL/min). The sample was then heated (from 25 °C to 750 °C with a heating rate of 5 °C/min) under hydrogen flow (50 mL/min). After 1 h at 750 °C, the heating was switched off and the reactor was purged with He (50 mL/min).

Oxidation states of the metallic species (Ni or Fe) were determined by Temperature Programmed Reduction measurements with a TPD/R/O 1100 device from CE instruments. 0.2 g of catalyst was placed in a quartz tube. The samples was then heated from 25 °C to 1000 °C with a heating rate of 2 °C/min and under 20 mL/min of a gas mixture (5 %vol. $H_2$ /95 %vol. $N_2$).

After the catalytic experiments, carbon deposits were estimated from thermogravimetric (TG) and differential scanning calorimetry (DSC) measurements, with a Sensys Setaram instrument. Samples were heated from 25 °C to 800 °C with a heating rate of 2 °C/min under air (20 mL/min). The curves are presented in Supplementary material.

### 2.3.Catalytic experiments

The catalytic experiments are performed on an experimental toluene reforming set-up, presented in Figures 2 and 3 (coming from previous work, Figures 1 and 2 in V. Claude *et al.* [42]). In order to prevent corrosion, the tubing is made of 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. A peristaltic pump (ISMATEC, Multi channels) is used for the water supply. Toluene is chemically incompatible with most of the polymeric tubes used in peristaltic pumps. Therefore, toluene is injected with a glass-PTFE syringe pump (KDScientific, Legato). Gases and liquids are 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 from condensation. At the outlet of the mixing chamber, the gas mixture is directed towards either the stainless steel reactor or the bypass line. The reactor is a quartz tube placed in an inox 316 tube with ½ inch intern diameter (Figure 3 from V. Claude *et al.* [42] ). An inner quartz reactor is used in order to avoid direct contact between the reactive gas mixture and the metallic reactor

at temperatures higher than 400 °C. Catalysts are placed in the quartz tube between 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 (Figure 3 from V. Claude *et al.* [42]), the catalytic samples are placed between 250 and 400 mm from the reactor bottom, *i.e.* in the homogeneous temperature zone.

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 gases ($CO_2$, CO, $H_2$, $N_2$) thanks to a backflush line with two analytic columns (Molsieve 5A and Porapak).

The catalysts are ground and sieved between 315 and 700 µm. The catalytic experiments are performed with a Gas Hourly Space Velocity (GHSV) of 6000 $h^{-1}$ (equivalent to a residence time of 0.6 s) and 250 mg of catalyst. The catalytic experiments are performed under operating conditions similar to the outlet of a steam reforming biomass fluidized bed gasifier [22] but with a fixed bed reactor. The reactant mixture consists in 31.5 %vol. $H_2$, 31.5 %vol. CO, 15.2 %vol. $CO_2$, 11 %vol. $H_2O$, 10 %vol. $CH_4$ and a toluene volume concentration of 8000 ppmv. With this gas mixture, the steam/carbon ratio is about 1. The catalytic performances of the samples are evaluated over 260 min with a GC injection every 15 min at both 750 °C and 850 °C. No pre-reduction step is carried out to activate the catalysts.

The toluene conversion, $C_T$, is calculated by Equation 1:

$$C_T = \frac{C_{T,In} - C_{T,Out}}{C_{T,In}} * 100 \quad (1)$$

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/$m^3$).

The benzene selectivity, $S_B$, is calculated by Equation 2:

$$S_B = \frac{C_{B,Out}}{C_{T,In} - C_{T,Out}} * 100 \quad (2)$$

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 calculated by Equation 3:

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

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$^3$).

Average values of $C_T$, $S_B$ and $C_{CH4}$ are calculated over the last 10 measurements of each experiment. In addition to the catalysts, the raw supports (alumina and olivine) are tested as well as inert quartz beads in order to determine the conversion reached in the absence of catalyst.

In order to assess the reusability of the catalysts, two successive catalytic experiments were performed on two samples: Ni2/$Al_2O_3$ and Ni2/Olivine. These two additional experiments were carried out at 750 °C in the same conditions as the first experiment (see above paragraphs).

## 3. Results and Discussion

### 3.1. Composition of the samples

Table 1 lists the theoretical and experimental compositions of the samples obtained by ICP measurements. The theoretical and actual compositions are similar for all samples. The high content of Fe (19.6 wt. %) in Fe10/Olivine is caused by the iron initially present in raw olivine

(7.8 wt. %). So the true Fe loading of this sample is actually 19.6-7.8 = 11.8 wt. %, which is satisfactory for a synthesis by wet impregnation.

### 3.2.Textural and physico-chemical properties of the samples

The specific surface area values, $S_{BET}$, the microporous volume, $V_{DR,}$ and porous volume values, $V_p$, of all catalysts are presented in Table 1. The doping of alumina with either Ni or Fe slightly reduces the specific surface area and microporous volumes (from 280 $m^2/g$ for pure $Al_2O_3$ to 265 $m^2/g$ and 220 $m^2/g$ for Ni- and Fe-doped alumina, respectively) but also slightly increases the porous volume values (from 0.4 $cm^3/g$ to 0.5 $cm^3/g$ and 0.7 $cm^3/g$). The nitrogen adsorption-desorption isotherms and the pore size distributions of these samples are very similar to those of pure $Al_2O_3$ as shown previously in [33]. The reduction of the microporous volume with the doping can come from the dopants which are probably less microporous than the pure alumina and which can blocked some micropores of the alumina [43].

Neither micro- nor mesoporosity is observed in the olivine samples ($S_{BET}$ < 1 $m^2/g$ and $V_p$ < 0.1 $cm^3/g$).

The TPR profiles of Olivine, Ni2/Olivine, Fe10/Olivine, Ni2/$Al_2O_3$ and Fe10/$Al_2O_3$ are shown in Figure 4a. The TPR profile of raw olivine (Figure 4a) shows a weak and broad $H_2$ consumption peak located between 500 °C and 900 °C. This peak is attributed to the reduction of iron species ($\alpha$-$Fe_2O_3$ and $MgFe_2O_4$), naturally present in the olivine, into $Fe_3O_4$ [22,24].

The TPR profile of Ni2/Olivine (Figure 4a) presents a reduction peak similar to the olivine sample, but also a very small peak located at 550 °C. This second peak is attributed to the reduction of a small amount of bulk nickel oxide (NiO) into metallic nickel. The quasi-absence of nickel reduction in this sample is due to the strong incorporation of Ni into the magnesium structure (formation of a spinel) [44]. The broad peak, attributed to the reduction of the Fe

species naturally present in raw olivine, is slightly shifted towards lower temperatures ($\Delta T \sim 50$ °C) for the Ni2/Olivine sample. This increased reducibility could be explained by the presence of metallic nickel $Ni^{(0)}$. Indeed, $Ni^{(0)}$ could promote the reduction of the iron oxide species by "spillover effects" of the $H_2$ molecules. This leads to the migration of the activated species ($H^*$) on distances up to micrometers. This explains why only a small amount of a dopant may greatly influence the reducibility of the catalyst [45,46].

In addition to the broad peak of the raw olivine, the TPR profile of the Fe10/Olivine sample (Figure 4a) presents a succession of peaks specific to the reduction of the additional Fe. The peak located at 430 °C is attributed to the reduction of iron oxide present at the surface of olivine ($\alpha$-$Fe_2O_3 \rightarrow Fe_3O_4$). As mentioned in the previous paragraphs, the second broad peak (500 °C – 700 °C) corresponds to the reduction of various iron oxides inside the Fe/olivine grain ($\alpha$-$Fe_2O_3$ or $MgFe_2O_4$). Finally, the last broad peak, between 700 and 1000 °C, is attributed to further reduction of iron species ($Fe_3O_4 \rightarrow Fe^0$) [22,24].

Regarding the Ni2/$Al_2O_3$ sample, the reduction of nickel only starts at 880 °C and is still under progress at 1000 °C (Figure 4a). This high reduction temperature points out the strong interactions between nickel atoms and alumina support. In that case, $Ni^{2+}$ ions are in a tetrahedral coordination and form a highly refractory nickel-aluminate ($NiAl_2O_4$) phase organized in a spinel structure [47–49]. Indeed, the percentage of reduced Ni during the TPR measurement is estimated to be only 20 %.

Fe10/$Al_2O_3$ sample (Figure 4a) presents three characteristic reduction peaks: i) the first peak, located at 415 °C, corresponds to the reduction of iron oxides with low interactions with the support ($\alpha$-$Fe_2O_3 \rightarrow Fe_3O_4$); ii) the broad reduction peak, between 500 °C and 800 °C, is attributed both to the reduction of iron oxides with strong interactions with alumina ($Fe_2O_3/Al_2O_3 \rightarrow Fe_3O_4/Al_2O_3$) and to the further reduction of the surface iron oxide species

($Fe_3O_4 \rightarrow FeO$); iii) the small peak observed at 875 °C could be due to the conversion of FeO species into metallic $Fe^{(0)}$ [50–52].

X-Ray diffractions (not shown here) were performed on all alumina-based materials after calcination (pure $Al_2O_3$, $Ni2/Al_2O_3$ and $Fe10/Al_2O_3$ samples). X-Ray patterns presents only the characteristic peaks of $\gamma$-$Al_2O_3$. In the case of the $Ni2/Al_2O_3$ sample, the small loading of Ni could explain the absence of visible NiO peak. In the case of the $Fe10/Al_2O_3$ sample, the absence of iron oxide peak after calcination can indicate a high dispersion of the iron dopant.

Figure 4b shows the X-Ray patterns of the alumina-based materials (pure $Al_2O_3$, $Ni2/Al_2O_3$ and $Fe10/Al_2O_3$ samples) after TPR measurements. The TPR analysis has no influence on the crystallinity of pure $Al_2O_3$ since characteristic peaks of $\gamma$-$Al_2O_3$ are still present. After TPR measurement, the $Ni2/Al_2O_3$ sample shows characteristic peaks of metallic nickel $Ni^{(0)}$. The $Fe10/Al_2O_3$ sample presents several peaks attributed to hercynite ($FeAl_2O_4$). However, no peak of metallic iron is observed after TPR measurement.

Figure 5a shows the X-Ray patterns of olivine before or after the TPR measurement. The X-Ray pattern of raw olivine presents typical peaks of calcined olivine, *i.e.* peaks of magnesioferrite ($(MgFe_2)O_4$) and forstierite ($(Mg_{1.85}Fe_{0.15})SiO_4$) [11,22,24]. The reduction during the TPR analysis led to an intense peak of metallic iron $Fe^{(0)}$ located at $2\theta = 44.8$ °. At $2\theta = 43.3$ °, the low intensity peak corresponds to iron oxide species partially reduced ($Fe_{0.289}O_{0.451}$). Figure 5b-c show the X-Ray patterns of the olivine catalysts doped with Ni or Fe after calcination. Both samples present typical peaks of calcined olivine, as observed in Figure 5a. In the case of the Ni2/Olivine sample, additional peaks of nickel oxide ($Ni_{3.75}O_4$) are present. In the case of the Fe10/Olivine sample, additional peaks of iron oxide ($Fe_2O_3$) and magnesioferrite ($(MgFe_2)O_4$) are observed. Figure 5d shows the X-Ray patterns of raw olivine and Ni2/Olivine after TPR measurements. After TPR, the Ni2/Olivine sample shows peaks of metallic nickel ($Ni^{(0)}$) at $2\theta = 44.6$ ° and $2\theta = 51.8$ °, and of an iron-nickel alloy mostly

composed of Fe at $2\theta = 65.0°$, called kamacite ($Fe_{0.96}Ni_{0.04}$). Figure 5e shows the X-Ray patterns of raw olivine and Fe10/Olivine after TPR measurements. The main differences between both patterns are: i) the presence of magnesium iron oxide ($(Mg_{0.9}Fe_{0.1})O$) peaks; ii) an increased intensity of the $Fe^{(0)}$ peaks (at $2\theta = 44.8$ °) in the Fe10/Olivine sample.

The sizes of the metallic nanoparticles after TPR measurements are presented in Table 1 for all samples: $d_{TEM}$ was determined from TEM pictures and $d_{XRD}$ from XRD measurements. The smallest Ni particle size ($d_{TEM}$ = 30 nm and $d_{XRD}$ = 23 nm) and associated standard deviation ($\sigma_{TEM}$ = 9 nm) are obtained for $Ni2/Al_2O_3$. On the contrary, raw olivine, Ni2/Olivine and Fe10/Olivine samples show large Ni and Fe particles. $d_{TEM}$ lies between 54 nm and 76 nm whereas $d_{XRD}$ lies between 29 nm and 43 nm. The difference between $d_{TEM}$ and $d_{XRD}$ is important for the olivine-based catalysts. But one has to note that huge standard deviations ($\sigma_{TEM}$ comprised between 33 nm and 98 nm) are associated to the mean value $d_{TEM}$. Furthermore, one large metallic particle observed by TEM may be formed from the agglomeration of several crystallites with different crystallographic orientations. Indeed, as depicted in Figure 6, the olivine-based samples show a large distribution of metallic ($Fe^{(0)}$ or $Ni^{(0)}$) nanoparticles size after TPR measurements. Nevertheless, the sizes of metallic particles presented in Table 1 are in agreement with the literature. Indeed, Virginie *et al.* [22] obtained $Fe^{(0)}$ nanoparticles with an average size lying between 34 nm and 45 nm for 10 wt. % Fe/Olivine catalysts. Meng *et al.* [53] observed iron nanoparticles between 54 and 97 nm for iron-doped olivine sample. Swierczynski *et al.* [11] obtained $Ni^{(0)}$ nanoparticles with an average size of about 20 nm for 3.9 wt. % Ni/Olivine catalysts. In Ashok *et al.* [54] and Charisiou *et al.* [55], they obtained $Ni^{(0)}$ nanoparticles of around 25 and 17 nm respectively.

The support (alumina or olivine) and the method of preparation (impregnation and sol-gel) affect the metallic particles sizes and their distribution. Two main reasons can explain the difference between both supports. On the one hand, unlike alumina, the olivine support does

not contain any micro- or mesoporosity (Table 1), which is known to play an essential role in the migration and coalescence of metallic crystallites [9,28,56]. On the other hand, the nickel and iron species have stronger interactions with alumina than olivine (Figures 4a and 4b). These high interactions can come from the preparation method. The olivine-based samples were prepared by impregnation so that the metallic species were deposited only at the surface of the non-porous olivine substrate. The $Al_2O_3$ based samples were prepared by a sol-gel process with a better dispersion of metallic species due to the precursor mixing. This is consistent with the reduction of Ni starting only at high temperatures (880 °C) for Ni2/$Al_2O_3$, whereas it starts at 550 °C for Ni2/Olivine. Furthermore, the metallic nanoparticles in the olivine samples are more mobile than the oxide nanoparticles [28,57] in the alumina samples. This would explain why the Ni nanoparticles supported on olivine are larger than the ones supported on alumina.

### 3.3. Catalytic activity and post-test characterizations

#### *3.3.1. Catalytic performances at 750 °C*

Figure 7a shows the toluene conversion at 750 °C as a function of time for the catalysts doped with Ni or Fe. Figures 7c and 7d show the benzene selectivity and the methane conversion for all samples. All catalytic performances (toluene conversion, $C_T$, benzene selectivity, $S_B$, methane conversion, $C_{CH4}$, $H_2$/CO molar ratio, carbon deposit amount after test, *Coke*) are listed in Table 2 for all samples and quartz.

**Raw supports**

At 750 °C (Table 2), raw olivine shows a better catalytic activity ($C_T$ = 31 %) than both pure $Al_2O_3$ ($C_T$ = 18 %) and quartz ($C_T$ = 5 %). Furthermore, olivine presents a lower benzene selectivity ($S_B$ = 19 %) than both pure $Al_2O_3$ ($S_B$ = 26 %) and quartz ($S_B$ = 79 %). However, at this temperature, the three samples produce methane (negative conversions values in Table 2). Due to the high selectivity towards benzene and the absence of coke after the test (*Coke* < 0.01

$g_{Carbon}/g_{Cata}$) for the raw supports, it is assumed that methane is mostly produced by hydrodealkylation reactions of toluene [58].

Two reasons could explain the good catalytic activity of $Al_2O_3$ and olivine compared to quartz (*i.e.* no catalyst): (i) the supports are able to adsorb toluene at their surface; (ii) the supports favor the adsorption-dissociation of $H_2O$ and $CO_2$ molecules necessary for the gasification reactions. This is attributed to the formation of (i) hydroxyl –OH groups in presence of water at the surface of $\gamma$-$Al_2O_3$ or (ii) MgO and $FeO_x$ species for raw olivine. Furthermore, isotope exchange studies showed that the dissociation of $H_2O$ is favored at the surface of MgO compared to $Al_2O_3$ [59]. This last observation could explain why the non-porous olivine showed more interesting $C_T$ and $S_B$ values than the mesoporous alumina.

**Ni-doped samples**

At 750 °C, the $C_T$ values stay constant during the catalytic experiment for both Ni2/$Al_2O_3$ and Ni2/Olivine (Figure 7a). This suggests that, in both cases, the catalysts keep the same active phases and crystallography during the whole experiment. Regarding the Ni-doping, Ni2/Olivine has better catalytic properties than Ni2/$Al_2O_3$ (Table 2): an almost complete conversion of toluene ($C_T$ = 99 % *vs.* $C_T$ = 77 %), a very low benzene selectivity ($S_B$ < 0.5 % *vs.* $S_B$ = 61 %), a high methane conversion ($C_{CH4}$ = 81 % *vs.* $C_{CH4}$ < 0.5%) and a good resistance against coking (*Coke* < 0.01 $g_{Carbon}/g_{Cata}$, *vs. Coke* = 0.05 $g_{Carbon}/g_{Cata}$).

These different catalytic activities between Ni2/$Al_2O_3$ and Ni2/Olivine samples lie in the different strengths of nickel/support interactions. Indeed, Ni contained in Ni2/$Al_2O_3$ sample is integrated into a stable and low catalytically active spinel structure ($NiAl_2O_4$) (Figure 4a). The X-Ray patterns of the alumina-based materials after a catalytic experiment at 750 °C are presented in Figure 8a. Neither bulk nickel oxide nor nickel metallic peak is present in Ni2/$Al_2O_3$. This confirms the presence of very strong interactions between Ni and alumina

(formation of spinel) [47–49,60]. On the contrary, Ni2/Olivine (Figure 8b) shows more catalytically active species such as partially reduced oxide (FeO), kamacite ($Fe_{0.96}Ni_{0.04}$) and metallic nickel ($Ni^{(0)}$). Indeed, such a high methane conversion and low benzene selectivity for Ni2/Olivine at 750 °C necessarily involves the presence of metallic species [11,28]. In Figure 8b, after the catalytic experiment at 750 °C, Ni2/Olivine presents very small peaks of FeO and kamacite ($Fe_{0.96}Ni_{0.04}$). Noteworthy, a characteristic peak of $Ni^{(0)}$ is also present. However, the peaks of bulk nickel oxide ($Ni_{3.75}O_4$) are always clearly visible.

The positive effect of the olivine support compared to the alumina support is clearly observed in Figure 7a. Indeed, a similar difference (around 10-15 %) in toluene conversion is observed between raw supports (olivine vs alumina) and Ni-doped supports (Ni2/Olivine vs $Ni2/Al_2O_3$).

Moreover, raw olivine naturally contains Fe. Therefore, the Ni-doped olivine could be considered as a bimetallic catalyst, leading to a better catalytic activity as observed in others studies with Ni-Fe catalysts [26,61].

**Fe-doped samples**

The $C_T$ values increase progressively during the catalytic experiment for $Fe10/Al_2O_3$ and Fe10/Olivine, as shown in Figure 7a. This observation suggests that the iron oxide species of both samples are reduced *in situ* during the catalytic test and are progressively more active during the tests. Indeed, the catalytic activity of iron oxide species generally increases with their reduction state ($Fe_2O_3 < Fe_3O_4 < FeO < Fe^{(0)}$) [29–32]. The Fe10/Olivine sample shows better catalytic properties than the $Fe10/Al_2O_3$ sample (Table 2): a higher toluene conversion ($C_T$ = 68 % *vs.* $C_T$ = 57 %), a lower benzene selectivity ($S_B$ = 6 % *vs.* $S_B$ = 19 %) and a higher methane conversion ($C_{CH4}$ = 4 % *vs.* $C_{CH4}$ = - 1 %).

The difference of catalytic activities is mostly attributed to difference of interactions between iron and each support. Indeed, in the case of Fe10/Olivine, the X-Ray pattern after the catalytic experiment (Figure 8c) reveals the presence of iron oxide species with different reduction states (FeO and $Fe_{0.92}O$), which are known to be beneficial to tar reforming reactions [22,29]. Noteworthy, the peaks of $Fe_2O_3$ observed after calcination have almost disappeared after the catalytic experiment at 750 °C. On the contrary, the X-Ray pattern of Fe10/$Al_2O_3$ (Figure 8a) only shows the presence of iron strongly incorporated into alumina (hercynite, $FeAl_2O_4$), which explains the lower toluene conversion and higher benzene selectivity for this sample. As for the Ni-doped samples, the difference between the two Fe-doped samples is similar than between the raw supports, highlighting the positive effect of olivine.

The Ni-doped samples have better activities than the iron ones, as reported in [53]. Indeed, Ni is more efficient for the reforming than Fe [27].

### *3.3.2. Catalytic performances at 850 °C*

Figure 7b shows the toluene conversion at 850 °C as a function of time for the catalysts doped with Ni or Fe. Figures 7c and 7d show the benzene selectivity and the methane conversion for all samples. All catalytic performances (toluene conversion, $C_T$, benzene selectivity, $S_B$, methane conversion, $C_{CH4}$, $H_2$/CO molar ratio, carbon deposit amount after test, *Coke*) are listed in Table 3.

**Raw supports**

At 850 °C (Table 3), toluene conversions are similar for raw $Al_2O_3$ and raw olivine ($C_T$ = 76 % and $C_T$ = 72 %, respectively) whereas $C_T$ = 39 % for quartz. However, the benzene selectivity is lower for raw olivine than for raw $Al_2O_3$ or quartz ($S_B$ = 27 % for olivine, whereas

$S_B$ = 55 % and $S_B$ = 43 % for $Al_2O_3$ and quartz, respectively). As observed at 750 °C, quartz, olivine and $Al_2O_3$ do not show any methane conversion and are almost free of carbon deposit after experiment (*Coke* ≤ 0.01 $g_{Carbon}/g_{Cata}$).

**Ni-doped samples**

Both Ni2/$Al_2O_3$ and Ni2/Olivine show a complete conversion of toluene, a very low benzene selectivity ($S_B$ < 0.5 %) and are almost free of carbon deposit after experiment (*Coke* < 0.01 $g_{carbon}/g_{cata}$) as shown in Table 3. However, the methane conversion is lower for Ni2/$Al_2O_3$ than for Ni2/Olivine ($C_{CH4}$ = 68 % *vs.* $C_{CH4}$ = 96 %).

The X-Ray patterns of the alumina-based materials after a catalytic experiment at 850 °C are presented in Figure 9a. The Ni2/$Al_2O_3$ sample does not present any nickel oxide or metallic nickel peaks. In that case, Ni atoms are so embedded in the spinel structure that they are not reduced even after a catalytic experiment at 850 °C.

In Figure 9b, peaks of FeO, kamacite ($Fe_{0.96}Ni_{0.04}$) and $Ni^{(0)}$ are observed on the X-Ray pattern of Ni2/Olivine after the catalytic experiment at 850 °C. It is assumed that the better catalytic performances of Ni2/Olivine are due to the presence of metallic nickel $Ni^{(0)}$ (Figure 9b).

However, higher temperatures seem favorable for Ni2/$Al_2O_3$, since interesting catalytic activity is obtained, though Ni atoms are still trapped in the $NiAl_2O_4$ spinel structure (Figure 9a) which is then the active phase in toluene reforming. The presence of this nickel-aluminate phase explains why Ni2/$Al_2O_3$ shows a much lower $C_{CH4}$ than Ni2/Olivine.

**Fe-doped samples**

The $C_T$ values increase progressively during the catalytic experiments at 850 °C, for Fe10/$Al_2O_3$ and Fe10/Olivine samples, as shown in Figure 7b. The conversion reaches almost 100% at the end of the experiments. Both samples show relatively low benzene selectivity ($S_B$ = 7 % and $S_B$ = 4 % respectively) and are almost free of carbon deposit after experiment (*Coke* < 0.01 $g_{carbon}/g_{cata}$). However, both samples present very low methane conversions compared to the Ni-doped samples ($C_{CH4}$ = 7 % and $C_{CH4}$ = 6 %). In the case of Fe10/$Al_2O_3$ (Figure 9a), the iron species are also integrated into the alumina support since the X-Ray pattern reveals characteristic peaks of hercynite ($FeAl_2O_4$). The X-Ray pattern of Fe10/$Al_2O_3$ sample also contains intense peaks of alumina corundum ($\alpha$-$Al_2O_3$) at $2\theta$ = 35.1 °/ 43.4 °/ 52.5 °/ 57.4 °/ 68.2 ° and 76.8 ° (Figure 9a). During the alumina phase transition, the alumina phases ($\gamma$, $\delta$, $\theta$-$Al_2O_3$), organized in a cubic system, are progressively converted into a stable hexagonal packing ($\alpha$-$Al_2O_3$) [62]. In this study, this phenomenon has a negative effect since the $\gamma$- to $\alpha$-$Al_2O_3$ phase transition leads to the loss of the advantageous micro- and mesoporosity of the $\gamma$-$Al_2O_3$ phase. For the iron oxides, this transformation occurs in a similar way, but the $\gamma$- to $\alpha$-$Fe_2O_3$ phase transition happens at much lower temperatures ($T_{\gamma\rightarrow\alpha\text{-}Fe2O3}$ ~ 350 °C, while $T_{\gamma\rightarrow\alpha\text{-}Al2O3}$ ~ 1000 °C). In the case of strong interactions between Fe and $\gamma$-$Al_2O_3$, $\alpha$-$Fe_2O_3$ can favor the transformation of cubic alumina towards hexagonal packing at lower temperatures [62]. Characteristic peaks of $Fe^{(0)}$ and FeO are observed in the X-Ray pattern of the Fe10/Olivine sample after catalytic experiment at 850 °C (Figure 9c). Despite the characteristic $Fe^{(0)}$ peaks (Figure 9c), the catalytic activity of Fe10/Olivine is similar to the one of Fe10/$Al_2O_3$, which only contains $FeAl_2O_4$. Finally, despite the phase transition in the Fe10/$Al_2O_3$ sample ($\gamma$- to $\alpha$-$Al_2O_3$) during the catalytic experiment, $C_T$ values remain stable after 4 h of experiment. This could be explained by the fact that, at high temperatures, the specific surface area of the supports becomes a much less important parameter [28,56].

**General comparison**

Regarding the toluene reforming, adding Ni instead of Fe and using Olivine instead of Alumina as support is an evident choice at least at lower temperature (750 °C instead of 850 °C). Regarding the methane reforming, the choice of Ni appears wiser at high temperature (850 °C).

Whatever the type of support or of dopant, all samples show very low amounts of carbon deposit after 4 h of catalytic experiment at either 750 °C or 850 °C. Several reasons could explain this fact: (i) the tests are performed at high temperatures ($T$ > 650 °C) favorable to the gasification of the carbon deposit; (ii) even at 850 °C, an important fraction of the metals (Ni or Fe) is not fully reduced. Although metallic oxides usually show lower reforming activities, they are much more resistant to carbon deposits [28]. Furthermore, it is reported that the incorporation of Ni inside $NiAl_2O_4$ spinel prevents sintering and the formation of carbon deposit [63].

### *3.3.3. Reusability experiments at 750°C*

The reusability of two samples, Ni2/$Al_2O_3$ and Ni2/Olivine, has been assessed at 750 °C. The catalytic results are presented in Figure 10. The toluene conversion, benzene selectivity and $CH_4$ conversion are compared with the results of the initial catalytic experiment presented in Figure 7. It is observed that each catalytic parameter stayed nearly constant between the three experiments, confirming the reusability of both catalysts. This is consistent with the low carbon contamination (Table 2), allowing to maintain a constant catalytic activity.

## 3.4.Comparison with literature

In this Section, the results obtained in this study are compared to other studies dealing with the catalytic reforming of tars. The large variability of conditions make it difficult to compare various studies (the catalyst synthesis and composition, the tar model molecule, the catalytic conditions such as temperature, pressure, reactor size, gas composition or type of reactor).

In Heo *et al.* [64], Ni-doped alpha-alumina, olivine or dolomite catalysts were prepared and modified with Ca, K and Mn. They tested the catalytic activities on the toluene (1000 ppm) reforming at 800 °C for 5 h. The toluene conversion was the highest for the dolomite samples reaching up to 65 % while it is around 20 % for the alumina and olivine samples. The conversions reached in our study are higher but the catalyst preparation is very different.

In Meng *et al.* [65], Fe-doped olivine samples were prepared. Different parameters were studied as the amount of Fe, the temperature of calcination and the addition of Ni. The catalytic experiments were performed in the range of 800-900 °C. The catalytic results showed a high toluene conversion (~ 100%), a very efficient carbon resistance and a catalytic activity stable for 48 h. The high conversion in this range of temperature is similar to the results of our study.

In Morin *et al.* [66], olivine samples were tested on the reforming of toluene in a fluidized reactor at 850 °C. They found that iron is more active towards tars removal when its oxidation state is low ($Fe^0$). This is consistent with our observations when comparing Fe/Olivine and Fe/$Al_2O_3$ samples. Similar observations were also found in [67].

## 4. Conclusions

In this work, $\gamma$-$Al_2O_3$ supports prepared by a new aqueous sol-gel synthesis were doped with either 2 wt. % of Ni or 10 wt. % of Fe for the bio-syngas purification. Commonly used olivine was also doped with either Ni or Fe by wet impregnation in order to compare their performances with the $\gamma$-$Al_2O_3$ based samples.

Nitrogen adsorption-desorption showed that alumina-based samples are highly porous materials (even for the doped samples) whereas the olivine-based samples do not present any specific surface area. The XRD patterns of the alumina-based samples showed that all the samples presented characteristic peaks of $\gamma$-$Al_2O_3$, the Ni-doped sample presented NiO peaks and the Fe-doped sample presented peaks of $FeAl_2O_4$. For the olivine-based samples, the XRD patterns highlighted the presence of olivine characteristic peaks in all cases, the Ni- and Fe-doped samples presented peaks of the corresponding metallic oxides (NiO and $Fe_2O_3$).

The catalysts were then tested on the toluene reforming at two different temperatures: 750 and 850 °C. At 750 °C, the nickel/olivine sample showed a better catalytic activity than the nickel/alumina sample. This lower activity was attributed to strong interactions between nickel and alumina (formation of a spinel $NiAl_2O_4$). Similarly, the strong interactions between iron and alumina (formation of hercynite $FeAl_2O_4$) explained also the lower catalytic activity for the iron/alumina sample compared to the iron/olivine one.

At 850 °C, the catalysts showed similar performances whatever the support (olivine or alumina). Both nickel-doped supports showed high toluene conversion, low benzene selectivity and were free of carbon deposits. However, due to lower interactions with the support, and a better reduction of Ni, the methane conversion was higher for the nickel/olivine sample. At this temperature, both iron/alumina and iron/olivine catalysts showed high toluene conversion, low benzene selectivity, but almost no methane conversion.

In conclusion, despite a lower dispersion of the metallic nanoparticles after reduction and the absence of porosity, olivine appears to be a more suitable primary catalytic support than alumina. This could be explained by the influence of the high temperatures used in the catalytic experiments. At high temperatures, the reaction kinetic is favored, becoming the predominant factor and overcoming the effect of porosity and specific surface area.

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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: Theoretical and actual compositions of the samples determined by ICP analysis.**

| Sample | $Al_2O_3$ (wt. %) | | $SiO_2$ (wt. %) | | MgO (wt. %) | | Ni (wt. %) | | Fe (wt. %) | | $S_{BET}$ | $V_{DR}$ | $V_p$ | $d_{TEM}$ | $d_{XRD}$ |
|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|---|
| | Theo. | Exp. | Theo. | Exp. | Theo. | Exp. | Theo. | Exp. | Theo. | Exp. | ($m^2\ g^{-1}$) ± 5 | ($cm^3\ g^{-1}$) ± 0.01 | ($cm^3\ g^{-1}$) ± 0.1 | (nm) | (nm) ± 1 |
| **$Al_2O_3$** | 100 | 100 | -[a] | -[a] | -[a] | -[a] | -[a] | -[a] | -[a] | -[a] | 280 | 0.11 | 0.4 | -[a] | -[a] |
| **Ni2/$Al_2O_3$** | 98.0 | 98.1 | -[a] | -[a] | -[a] | -[a] | 2.0 | 1.9 | -[a] | -[a] | 265 | 0.09 | 0.5 | 30 ± 9 | 23[b] |
| **Fe10/$Al_2O_3$** | 90.0 | 89.5 | -[a] | -[a] | -[a] | -[a] | -[a] | -[a] | 10.0 | 10.5 | 220 | 0.07 | 0.7 | -[a] | -[a] |
| **Olivine** | -[a] | -[a] | -[a] | 41.1 | -[a] | 51.1 | -[a] | -[a] | -[a] | 7.8 | < 1 | < 0.01 | < 0.1 | 54 ± 33 | 43[c] |
| **Ni2/Olivine** | -[a] | -[a] | -[a] | 38.9 | -[a] | 50.9 | 2.0 | 2.5 | -[a] | 7.7 | < 1 | < 0.01 | < 0.1 | 67 ± 75 | 29[d] |
| **Fe10/Olivine** | -[a] | -[a] | -[a] | 35.6 | -[a] | 44.2 | -[a] | -[a] | 17.8 | 19.6 | < 1 | < 0.01 | < 0.1 | 76 ± 98 | 42[c] |

$S_{BET}$: specific surface area determined by the BET method; $V_{DR}$: microporous volume calculated by the Dubinin-Raduskevitch method; $V_p$: specific liquid volume adsorbed at the saturation pressure of nitrogen; $d_{TEM}$: metallic particles size median; $d_{XRD}$: metallic crystallites size estimation obtained by XRD; [a]: not applicable; [b]: measured on the (2 0 0) ray of $Ni^{(0)}$ ; [c]: measured on the (1 1 0) ray of $Fe^{(0)}$; [d]: measured on the (1 1 0) ray of kamacite ($Fe_{0.96}Ni_{0.04}$).

**Table 2: Catalytic performances of catalysts with test conditions: $T$ = 750 °C, 8000 ppmv of toluene, $t$ = 4 h, $GHSV$ = 6000 $h^{-1}$.**

| Sample | $C_T$ (%) | $S_B$ (%) | $C_{CH4}$ (%) | $H_2/CO$ (-) | *Coke* ($g_{Carbon}/g_{Cata}$) |
|---|---|---|---|---|---|
| **Quartz** | 5 | 79 | - 3 | 0.96 | <0.01 |
| **$Al_2O_3$** | 18 | 26 | - 3 | 1.04 | <0.01 |
| **Ni2/$Al_2O_3$** | 77 | 61 | 0 | 0.94 | 0.05 |
| **Fe10/$Al_2O_3$** | 57 | 19 | - 1 | 1.03 | 0.02 |
| **Olivine** | 31 | 19 | - 2 | 1.03 | <0.01 |
| **Ni2/Olivine** | 99 | <0.5 | 81 | 0.99 | <0.01 |
| **Fe10/Olivine** | 68 | 6 | 4 | 1.00 | <0.01 |

$C_T$: conversion of toluene, $S_B$: selectivity in benzene; $C_{CH4}$: conversion of methane; $H_2$/CO: molar ration between $H_2$ and CO; *Coke*: amount of carbon deposit after 4 h of test determined by TG-DSC.

**Table 3: Catalytic performances of catalysts with test conditions: $T$ = 850 °C, 8000 ppm of toluene, $t$ = 4 h, $GHSV$ = 6000 $h^{-1}$.**

| Sample | $C_T$ (%) | $S_B$ (%) | $C_{CH4}$ (%) | $H_2/CO$ (-) | *Coke* ($g_{carbon}/g_{cata.}$) |
|---|---|---|---|---|---|
| **Quartz** | 39 | 43 | 0 | 0.93 | <0.01 |
| **$Al_2O_3$** | 76 | 55 | 1 | 0.92 | 0.01 |
| **Ni2/$Al_2O_3$** | 100 | <0.5 | 68 | 0.93 | 0.01 |
| **Fe10/$Al_2O_3$** | 99 | 7 | 7 | 0.91 | 0.01 |
| **Olivine** | 72 | 27 | -1 | 0.99 | <0.01 |
| **Ni2/Olivine** | 100 | <0.5 | 96 | 0.98 | <0.01 |
| **Fe10/Olivine** | 96 | 4 | 6 | 0.92 | <0.01 |

$C_T$: conversion of toluene, $S_B$: selectivity in benzene; $C_{CH4}$: conversion of methane; $H_2$/CO: molar ration between $H_2$ and CO; *Coke*: amount of carbon deposit after 4 h of test determined by TG-DSC.