

Synthesis of Ni/ γ -Al₂O₃-SiO₂ catalysts with different silicon precursors for the steam toluene reforming

Vincent Claude¹, Julien G. Mahy^{1*}, Jérémie Geens¹, Claire Courson², Stéphanie D. Lambert¹

¹Departement of Chemical Engineering - Nanomaterials, Catalysis and Electrochemistry, University of Liege, B6a, B-4000 Liège, Belgium

²Institut de Chimie et Procédés pour l'Energie, l'Environnement et la Santé, UMR CNRS 7515, University of Strasbourg, 25 rue Becquerel, 67087 Strasbourg, France

***Corresponding author: julien.mahy@uliege.be**, Tel: +32 4 366 95 34. Fax: +32 4 366 3545.

Abstract:

This work investigated the intrinsic properties and performances of Ni/ γ -Al₂O₃-SiO₂ modified with different silicon precursors for the steam reforming of toluene in biomass gasifier exit conditions (8000 ppmv of toluene, 650 °C). Samples were synthesized by an aqueous sol-gel process in presence of aluminum nitrate, nickel nitrate and the use of either tetramethoxysilane (TMOS, Si-(OCH₃)₄) or tetraethoxysilane (TEOS, Si-(OC₂H₅)₄) in order to understand the influence of the reactivity of the silicon precursor. Furthermore, the use of *N*-[3-(trimethoxysilyl)propyl]ethylenediamine (EDAS, (OCH₃)₃-Si-(CH₂)₃-NH-(CH₂)₂-NH₂) is also investigated in order to understand the influence of a silicon precursor containing an ethylenediamine group, able to complex Ni²⁺ ions.

By the chelation of Ni²⁺ ions by ethylenediamine groups during the synthesis, Ni/ γ -Al₂O₃-SiO₂ samples modified with EDAS showed higher dispersion of the metallic Ni nanoparticles and the higher resistance against the sintering of Ni particles. This was also attributed to the high microporous volume and the narrow mesoporous distribution of the support, which could also prevent the migration of the metallic Ni nanoparticles.

The catalytic tests revealed that the reactivity of the silicon precursor played a major role on the conversion of toluene. For alumina supports modified with a silicon precursor with a low reactivity such as TEOS, the low integration of the Si atoms inside the bulk alumina lead to a slightly higher catalytic activity, but also to a high formation of structured carbon. The opposite effect was observed for the samples modified with a highly reactive silicon precursor, such as TMOS or EDAS, which showed a slightly lower catalytic activity, but a higher resistance against coking compared to pure Ni/ γ -Al₂O₃ catalysts.

Keywords: Ni/ γ -Al₂O₃ catalysts; Sol-gel process; Syngas cleaning; tars reforming

1. Introduction

Among all the developed renewables energies, biomass gasification appears to be one interesting solutions for the upcoming energetic crisis [1]. The concept consists in the thermochemical conversion of biomass (wood pellets, dustsaw, energy crops, agricultural wastes,...) into valuable bio-syngas ($\text{CO} + \text{H}_2$). This bio-syngas can thereafter be directly burned, used in fuels cells or converted into various basics chemicals via the Fischer-Tropsch process. Therefore, this technology could provide an environmental friendly and sustainable source of energy.

Although current biomass gasification technologies can be extrapolate to large scales, some improvements still needs to be done in order to make these industrial plants more efficient and economically viable. Indeed, during the gasification steps, it is common that a part of the biomass is not fully converted into syngas but rather into aromatics compounds (tars) such as naphthalene or toluene [2]. These aromatic compounds cause various problems during downstream applications since they can condensate and therefore clog the pipes. Cleaning the final syngas from these undesirable compounds is thence essential. Among the different cleaning technologies, the use of catalysts to destroy the remaining tars appears to be the most interesting solution: there is no need to remove tars in downstream flows and the bio-syngas specific heat is increased due to the conversion of tars into CO and H_2 [3]. The catalyst is used either inside the reactor (primary catalyst) or directly at the outlet (secondary catalyst) [4].

Primary catalysts benefit from the high temperatures inside the reactors ($T > 800$ °C), but must exhibit a high attrition resistance since they are generally used in fluidized bed reactors. Usually cheap and natural materials doped with metals are used for this application [5]. In comparison, secondary catalysts have to work under different conditions. Due to the

lower temperatures at the exit of the gasifier reactors ($T = 500\text{-}700\text{ }^{\circ}\text{C}$), they need to exhibit higher catalytic performances and a longer life time. Indeed, at these lower operation temperatures, the catalysts are more inclined to be deactivated via carbon deposit mechanisms [5]. Furthermore, even if the intrinsic syngas composition is composed of reductive reagents (CO and H₂), the presence of oxidants (CO₂ and H₂O) prevents the reduction of the metallic active sites and therefore the regeneration of the catalytic cycle. Nevertheless, since the secondary catalysts do not undergo any mechanical stress, materials with a designed micro-, meso- and macro-structure can be used. Moreover, by their outlet position, these catalysts are able to be easily replaced and regenerated if deactivated via coking or poisoning by sulphidic phenomena [4-5].

Previous studies show that $\gamma\text{-Al}_2\text{O}_3$ appears as the best support for secondary catalysts [6, 7]. Indeed, Miyazawa *et al.* [6] present interesting catalytic properties of $\gamma\text{-Al}_2\text{O}_3$ for the steam reforming of tars derived from the pyrolysis of cedar wood. Furthermore, a comparison of the catalytic performances of nickel supported on $\gamma\text{-Al}_2\text{O}_3$ and SiO₂ for the reforming of toluene and naphthalene at temperatures similar to those encountered inside the gasifier reactor ($T = 730\text{-}850\text{ }^{\circ}\text{C}$) was made by Srinakruang *et al.* [8]. The authors showed that Ni/ $\gamma\text{-Al}_2\text{O}_3$ catalysts presented a higher catalytic activity compared to Ni/SiO₂ materials. The higher catalytic activity was notably attributed to the higher metal-support interactions of Ni/ $\gamma\text{-Al}_2\text{O}_3$ materials. Indeed, the strong interactions between Ni and $\gamma\text{-Al}_2\text{O}_3$ are known to prevent the sintering of the nickel nanoparticles and to afford a higher catalytic activity [9]. Furthermore, it is suspected that the simultaneous presence of metallic Ni⁰ particles and un-reduced spinel NiAl₂O₄ could favor a higher catalytic activity and a lower coking [9].

It is well-known that the catalytic activity depends on various intrinsic properties of the used materials (active site and support composition, porous structure and crystallography of the support...) [2]. Among them, the dispersion of the active sites and their interactions with the

support play a major role. When active sites are metallic particles, the active surface area, and thus the catalytic efficiency, increases when the size of metallic particles decreases. Furthermore, in the case of reforming reactions, it was shown that the rate of carbon deposition is proportional to the metallic nanoparticle diameter [10, 11]. Thus, below a critical size (~ 7 nm for Ni nanoparticles dispersed on Al_2O_3), the carbon deposit highly decreases and no filamentous carbon is supposed to be encountered.

Therefore, in the aim of obtaining finely dispersed metallic nanoparticles on the $\gamma\text{-Al}_2\text{O}_3$ supports, the use of a second support precursor, (i) able to chelate Ni^{2+} ions at the molecular level, and (ii) to react with the principal aluminum precursor by co-condensation reactions [12], must be used. Being that no commercial aluminum alkoxide with these properties are available, the use of a silicon alkoxide is necessary in this study. In previous studies [13, 14], *N*-(3-(trimethoxysilyl)propyl)ethylenediamine ($(\text{OCH}_3)_3\text{-Si-(CH}_2)_3\text{-NH-(CH}_2)_2\text{-NH}_2$, EDAS) has allowed obtaining very porous silica or titania catalysts, in which metallic or metallic oxide nanoparticles were highly dispersed. Indeed, the ethylenediamine groups contained in the functional chain of EDAS molecules were able to form a chelate with a metallic cation, thus increasing its dispersion at a molecular level inside the support. In the case of a complex formation between one ethylenediamine group and one Ni^{2+} ion at room temperature, the constant of formation and the enthalpy of formation are both high ($\text{Log}(K) = 7.5$ and $\Delta H_f^{298\text{K}} = -37.7 \text{ kJ/mol}$) [15]. Furthermore, Claude *et al.* [12] showed that the use of EDAS during the synthesis of a pure alumina support highly influences the textural properties of alumina and delays the γ - to $\alpha\text{-Al}_2\text{O}_3$ phase transition. It is why the use of two other silicon alkoxides will be investigated in this study in order to understand the influence of the reactivity of the silicon precursor on the physico-chemical properties of alumina: either tetramethoxysilane (TMOS, $\text{Si-(OCH}_3)_4$) or tetraethoxysilane (TEOS, $\text{Si-(OC}_2\text{H}_5)_4$). The innovation of this work lies the use of SiO_2 functionalization in $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ catalysts with cogelation process. Indeed, the use of

Al_2O_3 supports modified with chelating silicon precursors has been already studied in the literature [16]. However, the functionalization of $\gamma\text{-Al}_2\text{O}_3$ has always been performed by grafting methods, which are very different from the cogelation procedure used in this work.

2. Experimental

2.1 *Synthesis of Ni/ $\gamma\text{-Al}_2\text{O}_3\text{-SiO}_2$ catalysts*

Table 1 shows the operating synthesis variables for Ni/ $\gamma\text{-Al}_2\text{O}_3\text{-SiO}_2$ samples. The samples are named with the following criteria: “EDAS”, “TMOS” and “TEOS” prefixes refer to the silicon precursor used (EDAS, TMOS or TEOS). The amount of TMOS, TEOS or EDAS in samples (Table 1) is chosen in order to have 8.2 wt. % of SiO_2 after the calcination step in the catalyst. Finally, the prefix “10Ni” refers to the theoretical 10 wt. % of Ni obtained after the calcination and reduction steps. One additional sample, called 10Ni, is made of Ni/ $\gamma\text{-Al}_2\text{O}_3$ by NH_4OH precipitation without the use of a silicon precursor.

The syntheses are realized according to the following procedure: aluminum nitrate ($\text{Al}(\text{NO}_3)_3\text{*H}_2\text{O}$), distilled water, absolute ethanol and the silicon precursors (TMOS, TEOS or EDAS) are mixed together in a 500 mL bottle. The solutions are then stirred for 30 min. Thereafter, a precipitation step was performed by a dropwise addition (1 mL/min) of aqueous solutions of NH_4OH (15 M). As the pH increases, the solution becomes cloudy due to the aluminum hydroxide formation. When the pH reached 9.5, the vessel is then closed and set in the oil bath at 85 °C for 24 h under vigorous stirring. After that, the solutions are washed twice with water using a centrifuge (15 min, 10000 rpm), in order to remove the nitrate and ammonium compounds. The clean gels are afterwards re-dispersed into 100 mL of water during 30 min with vigorous stirring. Nickel nitrate ($\text{Ni}(\text{NO}_3)_2$) is then added to the solution and this

solution is mixed 30 min again. The mixture is placed into an oven for the first drying step at a temperature $T = 85^\circ\text{C}$ and pressure $P = 700$ mbar for 24 h. Thereafter, the samples are washed once with water and once with ethanol in order to evacuate the residual nitrate ions coming from $\text{Ni}(\text{NO}_3)_2$. It is to notice that the final washing is performed with ethanol to avoid the partial collapse of the mesopores during the drying step [17]. Thereafter, the gels are dried in an oven at $T = 110^\circ\text{C}$ for 24 h under $P = 900$ mbar. The dried monoliths are finally calcined under air for 5 h at the temperature $T = 550^\circ\text{C}$ with a heating rate of 2 $^\circ\text{C}/\text{min}$.

H_2 reduction steps are realized by putting 1 g of catalyst inside a cylindrical quartz tube inserted inside a metallic reactor, which was itself placed inside a tubular oven. The reactor is first purged with helium at room temperature (15 min, 50 mL/min), then a hydrogen flux is sent to the sample (50 mL/min) and the temperature is increased (from $T = 25^\circ\text{C}$ to $T = 750^\circ\text{C}$ with a heating rate of 5 $^\circ\text{C}/\text{min}$). After 1 h at 750°C , the heating is stopped and the reactor is purged with helium (50 mL/min) for 10 min.

2.2 *Characterization of $\text{Ni}/\gamma\text{-Al}_2\text{O}_3\text{-SiO}_2$ 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.

The conditions for the reduction of the Ni nanoparticles are provided by Temperature Programmed Reduction (TPR) tests which are realized with a TPD/R/O 1100 instrument. Samples are heated from 25 to 1000 $^\circ\text{C}$ with a heating rate of 2 $^\circ\text{C}/\text{min}$ and under a flow of 20 mL/min of 5 %vol. H_2 /95 %vol. N_2 .

Textural properties are determined thanks to nitrogen adsorption-desorption isotherms (BET) which are measured at -196 °C on a Micromeritics ASAP 2010 instrument after 12 h of outgassing at 300 °C and 10^{-5} Pa. The microporous volume, $V_{Dubinin}$, 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 [18].

The crystallographic properties of samples are determined by X-ray diffraction on a diffractometer Siemens D5000 (Cu- $K\alpha$ radiation) between 30° and 80° (2θ) with a step time of 18 s and a step size of 0.04 s. The sizes of Ni^0 particles are calculated by using the Scherrer equation centered on the Ni ray (2 0 0) ($2\theta = 51.83^\circ$) [19].

The sizes of Ni^0 particles and their distribution are also measured by transmission electron microscopy (TEM) performed on a CM10-PW6020 Philips Electron Microscope. 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).

The surface acidity measurements are realized with a Temperature Programmed Desorption (TPD) instrument. The measurements are realized according to the following steps: first, the samples are heated from 25 to 600 °C with a heating rate of 10 °C/min and under an air flow of 50 mL/min. These conditions are maintained for 1 h at 600 °C. Then, the samples are purged with a He flow of 50 mL/min and the heating is stopped until the temperature reached 100 °C. At 100 °C, an ammonia gas mixture (5 % vol. NH_3 /95 %vol. He) is injected with a flow-rate of 50 mL/min during 1 h. Thereafter, the sample is purged with 50 mL/min of He for 30 min. Finally, a slow heating rate is applied (2 °C/min, 100-600 °C) under He (50 mL/min). The TPD- NH_3 curves are determined from this last operating step.

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 to 800 °C with a heating rate of 2 °C/min under air (20 mL/min).

2.3 *Catalytic experiments on Ni/γ-Al₂O₃-SiO₂ catalysts*

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 $T = 180$ °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 $T = 400$ °C. Catalytic samples are 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 (CH₄,

toluene, benzene) with an analytic column (RTX1) and (ii) a TCD detector for the other gas (CO₂, CO, H₂, N₂) thanks to a backflush line with two analytic columns (Molsieve 5A and Porapak). It is also possible to quantify H₂O with the TCD detector. For both detectors, He is used as carrier gas.

The catalytic samples are crushed and sieved with a particle diameter distribution between 315 and 700 μm . The catalytic experiments are performed with two different Gas Hourly Space Velocities (GHSV): the first GHSV is set at 6000 h^{-1} (equivalent to a residence time of 0.6 s), for a mass of catalytic sample mass of 250 mg; the second GHSV is set at 24.000 h^{-1} (equivalent to a residence time of 0.15 s), for a mass of catalytic sample of 62.5 mg. The catalytic tests are realized with conditions similar to the outlet of a steam reforming biomass fluidized bed gasifier [20]. The reactant mixture consists in 31.5 %vol. H₂, 31.5 %vol. CO, 15.2 %vol. CO₂, 11 %vol. H₂O, 10 %vol. CH₄ and a toluene volume concentration of 8000 ppmv. The catalytic performances of the samples are evaluated for 300 min at 650 °C with a GC injection every 15 min. All calculated values (C_T , r_T , C_{CH_4} and S_B , see Equations 1-4 below) are obtained from the average of the GC concentrations of the last 150 min of the tests. It is to notice that no previous reduction step is realized to activate the catalysts. Furthermore, it is observed that the catalysts do not deactivate during the 150 min test length.

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

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

where $C_{T,\text{in}}$ is the initial toluene concentration (kmol/m^3) and $C_{T,\text{out}}$ is the toluene concentration at the outlet of the reactor (kmol/m^3).

The consumption rate of toluene, r_T ($\text{kmol/kg}_{\text{Ni}}\text{.h}$), is determined from the Equation 2 [21]:

$$r_T = \left(-\frac{F_T}{W} \right) \ln (1 - f_T) \quad (2)$$

where F_T is the molar flowrate of toluene at the reactor inlet (kmol/h), W is the nickel mass inside the reactor (kg_{Ni}) and f_T is the toluene conversion ($f_T = C_T/100$).

The methane conversion, C_{CH_4} , is determined from the Equation 3:

$$C_{CH_4} = \frac{C_{CH_4,In} - C_{CH_4,Out}}{C_{CH_4,In}} * 100 \quad (3)$$

where $C_{CH_4,in}$ is the initial methane concentration (kmol/m³) and $C_{CH_4,out}$ is the methane concentration at the outlet of the reactor (kmol/m³).

The benzene selectivity, S_B , is determined from the Equation 4:

$$S_B = \frac{C_{B,Out}}{C_{T,In} - C_{T,Out}} * 100 \quad (4)$$

where $C_{B,out}$ is the outlet concentration of benzene (kmol/m³), $C_{T,in}$ is the initial toluene concentration (kmol/m³) and $C_{T,out}$ is the toluene concentration at the outlet of the reactor (kmol/m³).

The tendency of producing coke during the catalytic tests, $Coke^*$ (g_{carbon}/g_T), is determined from the Equation 5:

$$Coke^* = \frac{Coke}{r_T * \left(\frac{\%Ni}{100}\right) * t * M_T} \quad (5)$$

where $Coke$ is the amount of carbon deposit determined from TG-DSC measurements (g_{carbon}/g_{Cata}), (%Ni/100) is the mass loading of nickel inside the catalyst (g_{Ni}/g_{cata}), determined from ICP-AES measurements, r_T is the consumption rate of toluene (mol_T/(g_{Ni}.h)), t is the time of test (h) and M_T is the molar mass of toluene (92.1 g_T/mol_T).

3. Results and Discussion

3.1. Composition of Ni/γ-Al₂O₃-SiO₂ catalysts

Table 2 shows the theoretical and actual loadings of samples determined by ICP-AES measurements. It is observed that the theoretical and actual values for Al_2O_3 , SiO_2 and Ni are similar.

3.2. Influences of silicon precursors on textural properties of $\text{Ni}/\gamma\text{-Al}_2\text{O}_3\text{-SiO}_2$ catalysts

Figure 3 shows the nitrogen adsorption-desorption isotherms and their associated mesopore size distributions for all calcined samples. The values of the specific surface area, S_{BET} , the specific liquid volume adsorbed at saturation pressure of nitrogen, V_p , and the microporous volume, V_{Dubinin} , are listed in Table 3.

All isotherms are characterized by a broad hysteresis characteristic of a nitrogen adsorption-desorption type IV isotherm according to the BDDT classification at pressures $p/p_0 > 0.4$ and a relatively important pore volume $V_p (> 0.05 \text{ cm}^3/\text{g})$ (Table 3). In Figure 3b, sample 10Ni presents a large mesoporous distribution (between 2 and 10 nm) centered on 7 nm. In Table 3, S_{BET} and V_{Dubinin} values are the lowest for sample 10Ni in comparison with the other samples, in which silica is present. Sample TEOS-10Ni shows the highest pore volume, V_p , which is equal to $0.7 \text{ cm}^3/\text{g}$. Furthermore, in Figure 3b, the mesopore size distributions of samples synthesized with TMOS and TEOS are very large from 2 nm to 25 nm. Sample EDAS-10Ni presents a very narrow mesopore size distribution, which is centered on 3 nm. This samples also exhibits the higher S_{BET} value ($450 \text{ m}^2/\text{g}$) and the higher V_{Dubinin} value ($0.14 \text{ cm}^3/\text{g}$) (Table 3).

The TEM observations on calcined samples (Figure 4) can be correlated to the forms of nitrogen adsorption-desorption isotherms (Figure 3a) and their respective pore size distributions obtained by the Broekhoff-de Boer method (Figure 3b) [18]. Samples TMOS-10Ni and TEOS-10Ni (Figure 4b,c) consist of a random gathering of $\text{Al}_2\text{O}_3\text{-SiO}_2$ layers-like crystallites, whereas

sample EDAS-10Ni (Figure 4a) presents $\text{Al}_2\text{O}_3\text{-SiO}_2$ grain-shape like crystallites, which leads to a neater layout of the crystallites. These observations are in accordance with a previous study [22] which highlighted that the EDAS templating effect is only due to its ethylenediamine chains and enables the formation of small and grain shaped $\text{Al}_2\text{O}_3\text{-SiO}_2$ nanocrystallites, and as a consequence a centered pore size distribution.

3.3. Acidity of $\text{Ni}/\gamma\text{-Al}_2\text{O}_3\text{-SiO}_2$ catalysts

Figure 5 presents the $\text{NH}_3\text{-TPD}$ curves performed on calcined samples. For each sample, a first desorption peak corresponding to weak acid sites is observed between $T = 100$ °C and $T = 400$ °C, followed by a second peak, between $T = 600$ °C and $T = 900$ °C, characteristic of stronger acid sites [23]. It was highlighted in [22] that the modification of $\gamma\text{-Al}_2\text{O}_3$ with different silicon precursors (EDAS, TMOS, TEOS ...) lead to modifications of the alumina crystallinity and to different degree of Si incorporation into the bulk alumina. Nevertheless, in Figure 5 and Table 4, all samples present similar TPD- NH_3 profiles and similar amounts of NH_3 desorbed ($\sim 0.5 \text{ mmol}_{\text{NH}_3}/\text{g}$). The similar values obtained for all the samples could be due to the low amount of SiO_2 loadings (around 8 wt.%). Noteworthy, this value of NH_3 desorbed is in the order of magnitude compared to the acidity of pure alumina and $\text{Al}_2\text{O}_3\text{-SiO}_2$ materials [23].

3.4. Reductibility and sizes of Ni nanoparticles in $\text{Ni}/\gamma\text{-Al}_2\text{O}_3\text{-SiO}_2$ catalysts

A simple reduction step (1 h, 750 °C, 5 °C/min, 100 %vol. H_2) is performed on all the samples to reduce nickel oxide nanoparticles into nickel nanoparticles in order to get information about the initial sizes of Ni nanoparticles. In parallel, Temperature-Programmed Reduction (TPR) measurements (2 °C/min, 25-1000 °C, 5 %vol. $\text{H}_2/95$ %vol. N_2) (Figure 6)

are also realized to study the nickel nanoparticles interactions with the Al_2O_3 - SiO_2 support and their resistance towards sintering at high temperature. After both thermal treatments, all the samples are analyzed by X-Ray diffraction (Figures 7 and 8). All samples present typical γ - Al_2O_3 peaks ($2\theta = 37.2^\circ/45.9^\circ/66.9^\circ$). The sizes of Ni^0 particles, d_{XRD} , are calculated by using the Scherrer equation centered on the Ni ray ($2\ 0\ 0$) ($2\theta = 53.5^\circ$) (Table 5) [19].

TEM measurements are also realized in order to determine the sizes of Ni^0 particles (Table 5). The mean diameter of Ni particles, d_{TEM} , and standard deviations, σ_{TEM} , are calculated from the diameters of 500 Ni^0 particles located in 5 different catalytic grains. From these measurements, the Ni^0 particle size distributions after the reduction step at 750 °C and after TPR measurements are presented in Table 5.

In Figure 6 are presented the TPR curves for all $\text{Ni}/\gamma\text{-Al}_2\text{O}_3\text{-SiO}_2$ catalysts. As each baseline coming back to its initial value at 1000 °C, it is assumed that the reduction of Ni species is complete for all the samples. The TPR profile of sample 10Ni shows a large peak from $T = 700$ °C to $T = 950$ °C, with a maximum set at $T = 850$ °C, characteristic of nickel oxide with strong interactions with the support such as NiAl_2O_4 [24]. It is observed that the reduction profiles of samples EDAS-10Ni, TMOS-10Ni and TEOS-10Ni are influenced by the nature of the silicon precursor used. In the case of a strong incorporation of Si atoms inside the bulk alumina (samples TMOS-10Ni and EDAS-10Ni), the reduction of NiAl_2O_4 is highly shifted toward lower temperatures ($\Delta T = -75$ °C or -50 °C). In contrary, when the incorporation of Si atoms inside the bulk alumina is less important (sample TEOS-10Ni), the shift of the Ni reduction is less important ($\Delta T = -25$ °C). This can be explained by the fact that NiO supported on pure SiO_2 is reduced at lower temperature ($T = 400\text{-}600$ °C) compared to when supported on $\gamma\text{-Al}_2\text{O}_3$ [25]. Consequently, a better incorporation of Si inside the bulk alumina could help to shift the reduction peak towards lower temperatures. The better reduction observed for sample EDAS-10Ni compared to sample TMOS-10Ni is explained by the fact that sample

EDAS-10Ni presents lower Ni particles sizes (Table 5). Indeed, it has been highlighted in [24, 25] that the smaller the Ni^0 particles are, the more reducible they are.

X-Ray diffraction measurements are performed on all calcined samples (not shown here) and only present $\gamma\text{-Al}_2\text{O}_3$ peaks, but no visible peaks of NiO or NiAl_2O_4 . This is assumed to be characteristic of a very fine dispersion of the nickel oxides on $\gamma\text{-Al}_2\text{O}_3$ and $\gamma\text{-Al}_2\text{O}_3\text{-SiO}_2$ supports. Figures 7 and 8 show the X-Ray diffraction patterns of the samples after H_2 reduction step and after TPR measurements. In both case, all X-Ray patterns present characteristic peaks of $\gamma\text{-Al}_2\text{O}_3$ and Ni^0 . Nevertheless, for samples EDAS-10Ni, TMOS-10Ni and TEOS-10Ni, the characteristic peaks of $\gamma\text{-Al}_2\text{O}_3$ are less defined compared to sample 10Ni. Indeed, Claude *et al.* showed that the incorporation of Si atoms inside the Al_2O_3 network delays the crystallization of amorphous alumina into $\gamma\text{-Al}_2\text{O}_3$ [22].

Table 5 shows the mean size of Ni^0 particles and their standard deviation for all samples after H_2 reduction and after TPR measurements. Even After H_2 reduction or TPR measurements, sample EDAS-10Ni shows the lowest Ni particle size ($d_{\text{XRD}} = 7 \text{ nm}$ and $d_{\text{TEM}} = 5 \text{ nm}$ after H_2 reduction and $d_{\text{XRD}} = 10 \text{ nm}$ and $d_{\text{TEM}} = 8 \text{ nm}$ after TPR measurement) and the lowest standard deviation value ($\sigma_{\text{TEM}} = 2 \text{ nm}$ after H_2 reduction and $\sigma_{\text{TEM}} = 3 \text{ nm}$ after TPR measurement). The Ni^0 particles sizes obtained for samples 10Ni, TMOS-10Ni and TEOS-10Ni are higher compared to sample EDAS-10Ni. So, during the synthesis step, thanks to the formation of complexes between the Ni^{2+} ions and the ethylenediamine groups of the chains of the EDAS molecules, these latter allow obtaining smaller Ni^0 nanoparticles homogeneously dispersed inside the $\text{Al}_2\text{O}_3\text{-SiO}_2$ support [13, 26, 27]. Furthermore, the Ni^0 particles sintering resistance of sample EDAS-10Ni could be correlated with the narrow porosity of this sample (micropores and very small mesopores $< 5 \text{ nm}$ (Figure 3)). Indeed, in samples 10Ni, TMOS-10Ni and TEOS-10Ni, the pore size distribution is larger (Figure 3b), thereby facilitating the mobility of the Ni^0 nanoparticles and their sintering.

3.5. Catalytic experiments on $\text{Ni}/\gamma\text{-Al}_2\text{O}_3\text{-SiO}_2$ catalysts

For the catalytic experiments, only calcined samples are used. Figure 9 shows the toluene conversion, C_T , as a function of time and Table 6 lists the catalytic performances of all samples at both $GHSV$ values (6000 h^{-1} and 24.000 h^{-1}). For all samples, C_T increases during the first 50 min of test due to the “*in situ*” reduction of the nickel active sites. After about $t = 50 \text{ min}$, C_T reaches a stable level until the end of the catalytic test.

At $GHSV$ of 6000 h^{-1} , sample Al_2O_3 shows very low C_T value (2 %), very high S_B value (15 %) and no methane conversion. In contrary, all catalysts (samples 10Ni, EDAS-10Ni, TMOS-10Ni and TEOS-10Ni) present high C_T values comprised between 82 and 94 %, low S_B values (< 4 %) and C_{CH_4} values comprised between 11 and 15 % (Table 6). So at $GHSV$ of 6000 h^{-1} , sample TEOS-10Ni shows the highest toluene reaction rate ($r_T = 1.2 \cdot 10^{-1} \text{ mol}_T/(\text{g}_{\text{Ni}} \cdot \text{h})$) and the highest methane conversion ($C_{\text{CH}_4} = 15 \text{ %}$). However, this sample also shows the highest benzene selectivity ($S_B = 4 \text{ %}$). Samples 10Ni, TMOS-10Ni and EDAS-10Ni show similar catalytic performances: r_T around $8 \cdot 10^{-2} \text{ mol}_T/(\text{g}_{\text{Ni}} \cdot \text{h})$, relatively low benzene selectivity ($S_B \sim 1\text{-}2 \text{ %}$) and $C_{\text{CH}_4} \sim 11\text{-}13 \text{ %}$.

It is observed that an increase of the $GHSV$ value from 6000 h^{-1} to 24.000 h^{-1} decreases the catalytic activity of all samples because of a lower time for the reactants and intermediate products to react together inside the catalytic reactor (the residence time is decreased from 0.6 s to 0.15 s). Globally, r_T is divided by a factor of about 3, S_B is increased by a factor of about 2 and C_{CH_4} is divided by a factor of about 2-3 (around 2 for samples 10Ni and TEOS-10Ni, and around 3 for samples TMOS-10Ni and EDAS-10Ni). It is observed that the sample EDAS-10Ni is the most affected by the increase of $GHSV$ (r_T is divided by 3.7 and C_{CH_4} is divided by 3.8) (Table 6). This sensitivity toward $GHSV$ is a consequence of the very narrow mesopore size

distribution of this sample (Figure 3), which could cause some diffusional limitations of the reagents at high *GHSV*. Indeed, Xu *et al.* [28] highlighted the importance of pores with sufficient sizes in tars reforming catalysts: pores diameters < 2 nm are useless for this application since common tar molecule size is situated around 0.5-1 nm (toluene: 0.68 nm; naphthalene: 0.72 nm). In opposite, in Ni/ γ -Al₂O₃ catalysts doped with TMOS and TEOS, the pore size distribution is very large, which could explained the higher catalytic activity, even at high *GHSV*. However, it is important to notice that Ni/ γ -Al₂O₃ catalysts doped with TMOS or TEOS also present higher S_B values, meaning that though their toluene conversion are high, their performances to break the aromatic ring are lower.

Figure 10 shows the DSC measurements performed after the catalytic tests under air. It is observed that for *GHSV* of 6000 h⁻¹, sample 10Ni presents a first peak between 300 °C and 500 °C, characteristic of the combustion of amorphous carbon, and a second large peak between 450 °C and 650 °C, characteristic of the combustion of structured carbon (carbon nanotubes) [29]. However, in Table 6, sample 10Ni shows a high tendency to form carbon deposit (*Coke** = $8.6 \cdot 10^{-2}$ g_{Carbon}/g_T). In comparison, samples EDAS-10Ni and TMOS-10Ni are less inclined to form carbon deposit (*Coke** = $3.6 \cdot 10^{-2}$ g_{Carbon}/g_T for sample EDAS-10Ni and *Coke** = $4.0 \cdot 10^{-2}$ g_{Carbon}/g_T for sample TMOS-10Ni) and present the lowest *Coke* values after the catalytic tests (around 0.10-0.15 g_{carbon}/g_{cata}) (Table 6). Nevertheless, some differences exist between samples EDAS-10Ni and TMOS-10Ni. Indeed, in Figure 10a-b, sample EDAS-10Ni presents a very large combustion peak from 400 °C to 600 °C, characteristic of the combustion of amorphous carbon [29]. In opposite, sample TMOS-10Ni presents two large peaks from 500 °C to 650 °C, characteristic of the combustion of structured carbon [29]. So the nature of carbon (amorphous or structured) formed during the catalytic test is strongly influenced by the nature of the silicon precursor. Indeed, in Figure 3b, it is observed that the distribution of the pore sizes is very narrow and centered around 3 nm for sample EDAS-10Ni, while the distribution of the pore

sizes is large (from 3 to 15 nm) for sample TMOS-10Ni. Furthermore, in Figure 4 (TEM observations), the Al_2O_3 - SiO_2 elementary particles are spherical in sample EDAS-10Ni, while these Al_2O_3 - SiO_2 elementary particles have the form of needles in sample TMOS-10Ni. Finally, the size of Ni^0 nanoparticles are lower in sample EDAS-10Ni compared to sample TMOS-10Ni (Table 5). It was shown [28-30] that more larger metallic nanoparticles favor the coking and the formation of structured carbon such as carbon nanotubes. So when structured carbons are formed, the regeneration operation becomes more difficult. So, EDAS-10Ni presented the best carbon deposition resistance.

Sample TEOS-10Ni presents the highest tendency to form carbon deposit ($\text{Coke}^* = 1.1 \cdot 10^{-1} \text{ g}_{\text{Carbon}}/\text{g}_{\text{T}}$) and the largest amount of carbon deposit after test ($\text{Coke} = 0.61 \text{ g}_{\text{Carbon}}/\text{g}_{\text{Cata}}$). Furthermore, DSC (Figure 10) and TEM measurements (Figure 11) reveal that the carbon deposit of this sample is composed of carbon nanotubes.

All these results can be correlated to the work of Srinakruang [30], which observed that after 6 h of steam reforming of a tar mixture (toluene + naphthalene) at $T = 770 \text{ }^\circ\text{C}$, the Ni/SiO_2 catalysts showed a carbon deposit amount four times higher than the $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ catalysts. Furthermore, always in the same study [30], TG-DSC measurements performed after the catalytic tests revealed that the carbon deposits were more amorphous for the $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ catalysts ($T_{\text{combustion}} = 400\text{-}750 \text{ }^\circ\text{C}$) and more structured (carbon nanotubes) for the Ni/SiO_2 catalysts ($T_{\text{combustion}} = 540\text{-}750 \text{ }^\circ\text{C}$).

In this study with the conditions of catalytic tests of toluene reforming, a better incorporation of the Si atoms inside the bulk alumina, provoked by a highly reactive silicon precursors (EDAS or TMOS), results in catalysts with a slightly lower catalytic activity than the standard $\text{Ni}/\gamma\text{-Al}_2\text{O}_3$ catalyst (sample 10Ni), but which present a more marked resistance against coking. In opposite, the modification of the $\gamma\text{-Al}_2\text{O}_3$ support with a low reactive silicon precursor (TEOS) led to catalysts with slightly higher toluene and methane conversions, but

with a higher benzene selectivity and which were more sensible toward coking. It is assumed that, in that case, SiO_2 is not fully integrated inside the bulk alumina and led to a higher amount and more stable carbon deposit as in the case of Ni/SiO_2 catalysts [30].

It is observed for all samples, that an increase of $GHSV$ decreases the catalytic activity, but lead to similar amount and type of carbon deposit after catalytic tests (Table 6, Figure 10). Consequently, the tendency to form coke increases with $GHSV$ (Coke^* values about 2-3 times higher when $GHSV$ increases from 6000 h^{-1} to 24.000 h^{-1}). This observation is important since usually an increase of $GHSV$ allows a lower carbon deposit due to the lower catalytic activity and to the lower time for the carbon atoms to transform into stable carbaceous species [29]. Nevertheless, the results of the present study is compared to the work of Da Silva *et al.* [31], who performed the steam reforming of ethanol at $T = 500 \text{ }^\circ\text{C}$. The authors highlighted that during reforming reactions, the relation between the space ratio and the amount of carbon deposit was absolutely not linear and not predictable. In this way, the authors observed that the amount of carbon deposit increased with $GHSV$ until reaching a maximum value. Further increase of $GHSV$ led to a decrease of the carbon deposit amount, and finally to a standard value. According to the same authors, the cracking of the ethanol molecule occurs quickly, but the mechanism of carbon removal which includes the diffusion of the oxidant species (O^* , HO^*) from the support surface to the metallic particle requires long contact time. In the present case, it appears that both $GHSV$ are situated in the range where the carbon deposit rate reaches a standard value, which explains why a modification of the space time modifies the toluene conversion but has little effects on the coking. In view of these results, it seems more interesting to perform the next catalytic tests of toluene reforming at $GHSV$ of 6000 h^{-1} instead of 24.000 h^{-1} .

4. Conclusions

This study compared the catalytic performances of 10 wt.% Ni/ γ -Al₂O₃ materials modified with different type of silicon precursors (TMOS, TEOS and EDAS) for the reforming of 8000 ppmv of toluene at $T = 650$ °C.

By the formation of EDAS/Ni²⁺ complexes during the synthesis, alumina modified with EDAS allowed obtaining a better initial dispersion of the metallic Ni particles. So Ni/ γ -Al₂O₃-SiO₂ catalysts modified with EDAS showed the highest resistance against the sintering of Ni particles. This was attributed to the high microporous volume and the narrow mesoporous distribution of the support, which decrease the migration of the metallic Ni crystallites.

The catalytic tests revealed that the reactivity of the silicon precursor played a major role on the conversion of toluene. For alumina supports modified with a silicon precursor with a low reactivity such as TEOS, the poor integration of the Si atoms inside the bulk alumina led to slightly higher catalytic activities, but also to a high formation of structured carbon such as carbon nanotubes. This was explained by the fact that Ni/SiO₂ catalysts are known to be more sensible against coking than Ni/ γ -Al₂O₃ catalysts. The opposite effect was observed for the samples modified with a highly reactive silicon precursor, such as TMOS or EDAS, which showed slightly lower catalytic activities, but also better resistances against coking than pure Ni/ γ -Al₂O₃ and TEOS doped catalysts. These catalysts seems to be promising materials to operate during longer duration.

Finally, it was observed for all samples that a higher *GHSV* led to a lower catalytic activity, but also to a higher tendency to form carbon deposit. This was assumed to be caused by the fact that, whereas the cracking of the toluene at the surface of the Ni particles is relatively quick, the dissociation of the H₂O and CO₂ molecules, and the migration of their oxidative species (O* and HO*) from the support to the carbonaceous compounds situated at the surface

of the Ni particles requires a longer contact time. In this way, it seemed more appropriate to keep a *GHSV* of about 6000 h⁻¹ for the future catalytic tests.

Acknowledgments

V. Claude thanks to F.R.S.-F.N.R.S. for his doctoral grant obtained with the “Fonds de Recherche collective” n° 2.4541.12. S. D. L. is also grateful to F.R.S.-F.N.R.S for her Research Associate position. The authors also acknowledge the Ministère de la Région Wallonne Direction Générale des Technologies, de la Recherche et de l’Energie (DG06) for financial supports.

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