# Enhancement of the catalytic performances and lifetime of Ni/$\gamma$-$Al_2O_3$ catalysts for the steam toluene reforming via the combination of dopants: Inspection of Cu, Co, Fe, Mn and Mo species addition

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## Abstract

In this work, the influence of metallic dopant addition in 10 wt. % Ni/$\gamma$-$Al_2O_3$ catalyst were studied on the material physico-chemical properties and catalytic activity for the toluene steam reforming. Seventeen doped Ni/$\gamma$-$Al_2O_3$ catalysts were synthesized by sol-gel process. The aim of the study was to determine which elements were the most performing for the doping of 10 wt. % Ni/$\gamma$-$Al_2O_3$ catalysts. The influence of the dopants were studied through different physico-chemical techniques. It appeared that some dopants showed lower catalytic performances due to high carbon deactivation. Contrarily, some dopants increased the resistance to coking while also improving the catalytic activity. Different mechanisms were proposed to explain these modifications of catalytic behavior. Among all doped Ni/$\gamma$-$Al_2O_3$ catalysts, the samples which combined Mn+Mo or Co+Mo dopants showed the most performing catalytic performances at 650 °C. Both samples showed high toluene reforming activity and low amounts of carbon deposit.

## 1. Introduction

The production of syngas from biomass becomes an interesting way to valorize some organic waste. Indeed, from this syngas, it is possible to produce valuable chemicals or use it as combustible [1,2]. The major challenges concern the bio-syngas reactors which can face some technical problems such as reactor fouling and clogging due to tars formation [1–4].

The development of catalytic reforming of these tars has shown to be a possible practical and economical solution [1–3,5–10]. The study of efficient catalysts for reforming had rapidly emerged. Different configurations can be envisaged for bio-syngas reactors which will influence the required catalyst properties. Indeed, if the catalyst is located in the reactor (primary catalyst), it will process in fluidized bed conditions. An important catalyst mechanical resistance will be needed. While, if the catalyst is placed at the outside of the reactor (secondary catalyst), lower temperature reactions (~650 °C) will occur and no mechanical stress will be applied. This work will focus on secondary catalysts.

For now, Ni catalysts are referenced as the most efficient materials for tars reforming with loadings around 15-20 wt% [1]. Practically, this active phase is deposited on a metallic oxide material as $Al_2O_3$, $ZrO_2$, Zeolites or Olivine. $\gamma$-$Al_2O_3$ supports are underlined as the most efficient supports for secondary catalyst applications [1,2,5,10,11].

The addition of elements interacting with the metallic active site, the catalytic support or both, is a common and easy way to improve the catalytic performances of a material. The reviews of Chan *et al.* [3], Anis *et al.* [5] and Yung *et al.* [10] give an overview of the numerous studies for the development of tar reforming catalysts. Among them, nickel and alumina, promoted thanks to different metals or oxides, appear as the most interesting types of catalysts. In the case of reforming catalysts, the two major criteria of a dopant lie in its ability to increase the catalytic conversion and to decrease the coking of the catalyst. Furthermore, other properties are usually targeted such as a better selectivity, an enhancement of the $H_2/CO$ ratio, an improvement of the conversion of $CH_4$ and a prevention of the formation of filamentous carbon. Obviously, the doping of the catalyst must not alter the standard properties such as the crystallinity or the specific surface area of the support. Nevertheless, the variability of the synthesis procedures (*i.e.* impregnation *vs.* sol-gel, conditions of calcination) and the numerous conditions of catalytic tests applied among the studies (*i.e.* type of tar, concentration of tar, $H_2O/C$ ratio, $CO_2/C$ ratio, temperature, *GHSV*, gas mixture, duration of test) make the comparison of the results very difficult. .

The use of bimetallic nickel/alumina as reforming catalysts has shown very good performances in terms of catalytic activity and/or catalyst lifetime [3,12–17]. Many studies highlighted the beneficial effect of noble metal addition (*e.g.* Pt, Ru, Rh or Ir) on nickel-based catalysts used for the reforming of tars [18–22]. However, the high prices of these elements make them economically inadequate for the development of catalysts intended for the purification of biomass gasifier tars. On the other hand, the association of Ni with more affordable metals such as Cu, Co, Fe, Mn or Mo have also proved to be beneficial for reforming applications. Moreover, from previous work on $MgAl_2O_4$ [23–25], it is likely that $NiAl_2O_4$ could stabilize the dopant metal in the form of single atoms and small clusters. This stabilization effect could mitigate the coke formation and so enhance the catalytic activity. In the search of new trends and new properties, trimetallic catalysts (Ni + metal n° 1 + metal n° 2) are also studied in this work. The literature about such catalysts is almost nonexistent, and some properties exhibited by these catalysts remain unclear.

So, this work consists in the characterization and testing of catalysts at 650 °C for the reforming of 24.000 ppmv of toluene. 10 wt. % Ni/$\gamma$-$Al_2O_3$ catalysts were doped with 2 wt. % of metal (*i.e.* Cu, Co, Fe, Mn or Mo). Looking for synergistic influences, it was also decided to study 10 wt. % Ni/$\gamma$-$Al_2O_3$ catalysts doped with 2 wt. % of two different metals. In view of the result obtained, it was also decided to dope 10 wt. % Ni/$\gamma$-$Al_2O_3$ catalysts with 4 wt. % of the most promising metals (Mn and Mo). The influence of the dopants on the physico-chemical and catalytic properties were studied thanks to X-ray diffraction, nitrogen adsorption-desorption isotherm, inductively coupled plasma–atomic emission spectroscopy, transmission and scanning electron microscopy, temperature programmed reduction measurements, and thermogravimetric and differential scanning calorimetry measurements.

## 2. Materials and Methods

### *2.1. Synthesis of doped Ni/$\gamma$-$Al_2O_3$ catalysts*

The catalysts were prepared according to the sol-gel aqueous method used in Claude *et al.* [26]. The alumina hydroxide sol was prepared and washed two times with water, then $Ni(NO_3)_2$ was added, followed by the addition of further dopants. Most of the doping were performed with nitrate salts of formulae $M(NO_3)_x.nH_2O$, where M is Cu, Co, Fe or Mn. For Mo, the doping was performed with molybdic acid salt ($MoO_3{\cdot}H_2O$). After the addition of salts, the sol was stirred for 30 min and put into an oven for classic drying steps: 24 h at 85 °C under 700 mbar, and then 24 h at 110 °C under 900 mbar. Finally, the dried samples were calcined under air for 5 h at 550 °C with a heating rate of 2 °C/min.

Simple doped catalysts were composed of $\gamma$-$Al_2O_3$, 10 wt. % of Ni and2 wt. % of metal (*i.e.* Cu, Co, Fe, Mn, Mo).

Influence of the element loading was studied with catalysts composed of $\gamma$-$Al_2O_3$, 10 wt. % of Ni and 4 wt. % of the best metals (*i.e.* Mn and Mo).

Double doped catalysts were composed of $\gamma$-$Al_2O_3$, 10 wt. % of Ni and 2 wt. % of two different metal dopants (*i.e.* Cu, Co, Fe, Mn, Mo).

The samples were named with the metal species present in the material with its percentage. For example, 10 wt. % Ni/$\gamma$-$Al_2O_3$ with 2 wt. % Cu sample was denoted 10Ni-2Cu. The amount of reagents were denoted in Supplementary Materials in Table S1.

### *2.2.Characterizations*

Samples compositions are determined by inductively coupled plasma–atomic emission spectroscopy (ICP–AES), equipped with an ICAP 6500 THERMO Scientific device [26]. Solid samples are crushed and then dissolved with lithium tetraborate before analysis. Aluminum, and nickel loadings are obtained by comparison with standard solutions in the same medium [26].

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 [26]. The microporous volume, $V_{DR}$, is calculated by the Dubinin-Raduskevitch method on the first branch of the adsorption curves at low relative pressure ($p/p_0 < 0.4$) [26]. The pore size distributions are determined by the Broekhoff de Boer method (BdB) applied to the adsorption profile-branch of the nitrogen isotherm [27].

The crystallographic properties of samples are 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° [26]. The alumina crystallite sizes were calculated by using the Scherrer equation centered on the (4 0 0) ray $\gamma$-$Al_2O_3$ (*i.e.* $2\theta = 67.0°$) of the XRD pattern [26]. The $Ni^{(0)}$ crystallite sizes were calculated by using the Scherrer equation centered on the (2 0 0) ray (*i.e.* $2\theta = 51.83°$). The size of the crystallites of the Ni-M alloys (M = Cu, Fe, Co, Mn or Mo) were determined by using the Scherrer equation centered on the Ni-M (2 0 0) ray. The

$Mo^{(0)}$ particles sizes were calculated on the Mo (2 1 1) ray (*i.e.* $2\theta = 73.70°$). The $Cu^{(0)}$ particles sizes were calculated on the Cu (2 0 0) ray (*i.e.* $2\theta = 50.48°$).

The size of metallic particles and their distribution are measured by transmission electron microscopy (TEM) performed on a CM10-PW6020 Philips Electron Microscope with measurements on around 100 particles on TEM micrographs [26]. First, powdered 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) [26].

$H_2$ reduction steps were performed on 1 g of sample [26]. The reactor was first purged with helium at room temperature (15 min, 50 mL/min). Then, a hydrogen flux was sent 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) [26].

Temperature Programmed Reduction measurements were performed with a TPD/R/O 1100 device from CE instruments to give information about the reduction of the metallic species present in the samples [26]. An amount of 0.2 g of catalyst was placed in a quartz tube. 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.% $N_2$) [26].

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) [26].

### *2.3. Catalytic experiments*

The samples were tested at 650 °C, for 300 min, with a standard procedure described in [26,28], with a toluene concentration of 24,000 ppmv and a gas mixture of 31.5 %vol. $H_2$, 31.5

%vol. CO, 15.2 %vol. $CO_2$, 11 %vol. $H_2O$, 10 %vol. $CH_4$. The mass of the catalyst was set to 300 mg, for a catalytic bed height of 12 mm, with a gas flowrate of 50 mL/min and consequently a *GHSV* of 5000 $h^{-1}$ (residence time of 0.72 sec) [26]. The following formula are identical to those from [26,28]:

The toluene conversion, $C_T$, is determined from the Equation 1 [26]:

$$C_{\mathrm{T}} = \frac{C_{\mathrm{T,In}} - C_{\mathrm{T,Out}}}{C_{\mathrm{T,In}}} * 100 \tag{1}$$

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/$m^3$) [26].

The benzene selectivity, $S_B$, is determined from the Equation 2 [26]:

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

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/$m^3$) [26].

The methane conversion, $C_{CH4}$, is determined from the Equation 3 [26]:

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

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/$m^3$) [26].

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 [26].

The consumption rate of toluene, $r_T$, in $mol_T/(g_{Ni}.h)$, was also compared [26]. 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 [26]. 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 [26]:

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

where $r_{\mathrm{T}}$ is the consumption rate of toluene ($\mathrm{mol_T/(g_{Ni}.h)}$), $k$ is the apparent kinetic constant ($\mathrm{m^3/(g_{Ni}.h)}$), and $C_{\mathrm{Tolu}}$ is the concentration of toluene ($\mathrm{mol_{Tolu}/m^3}$) [26].

Since the reaction rate is assumed to be of first order (n = 1), $r_{\mathrm{T}}$ can also be expressed as follows [29,30] [26]:

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

where $F_{\mathrm{T}}$ is the molar flowrate of toluene at the reactor inlet ($\mathrm{mol_T/h}$), $W$ is the nickel mass inside the reactor (g), and $f_{\mathrm{T}}$ is the toluene conversion ($f_{\mathrm{T}} = C_{\mathrm{T}}/100$) [26].

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 6 [26]:

$$Coke^{*} = \frac{Coke}{r_{\mathrm{T}} * \left(\frac{\%Ni}{100}\right) * t * M_{\mathrm{T}}} \tag{6}$$

where *Coke* is the amount of carbon deposit determined from TG-DSC measurements ($\mathrm{g_{Carbon}/g_{Cata}}$), ($\%Ni/100$) is the mass of nickel per unit mass of catalyst ($\mathrm{g_{Ni}/g_{catalyst}}$), determined from ICP-AES measurements, $r_{\mathrm{T}}$ is the consumption rate of toluene ($\mathrm{mol_{Tolu}/(g_{Ni}.h)}$), $t$ is the time of test (*i.e.* 5 h), and $M_{\mathrm{T}}$ is the molecular mass weight of toluene (*i.e.* 92.1 g/mol) [26].

## 3. Results and Discussion

### *3.1. Catalysts doped with 2 wt. % of metal*

#### 3.1.1. Composition and textural properties

Table 1 shows the composition of 10 wt. % Ni/$\gamma$-$Al_2O_3$ catalysts prepared with 2 wt. % of metal. The theoretical and actual loadings are similar for all samples. Table 1 shows also the textural properties ($S_{BET}$, $V_p$, and $V_{DR}$). All samples are micro- and mesoporous. Furthermore, at these low loadings, the element doping has no visible influence on the textural properties of the samples. Consequently, it is assumed that the textural properties are relatively similar for all samples and that the differences of catalytic performances exhibited are only attributed to the different nature of the dopant.

### 3.1.2. Crystallinity, particle size and reducibility

Figure 1 presents the reduction profiles and the X-Ray patterns after TPR for 10Ni, 10Ni-2Mo, 10Ni-2Mn, 10Ni-2Cu, 10Ni-2Co, and 10Ni-2Fe samples. Figure 2 presents some TEM micrographs for three samples after TPR as examples, all samples had similar aspects (highly dispersed metallic nanoparticles into alumina matrix) with only variation in the Ni nanoparticles size. Table 2 presents the metallic particle size and the eventual presence of Ni-M alloys (*i.e.* M = Cu, Fe, Co, Mn or Mo) determined after TPR measurements by TEM and XRD analyses.

The TPR profile of 10Ni-2Mo sample (Figure 1a) shows three reduction peaks: i) one peak located at about 430 °C, attributed to the reduction step of Mo oxides with low interactions with the support (*i.e.* $MoO_3 \rightarrow MoO_2$); ii) a second peak located at about 550 °C, attributed to the reduction of Mo oxides with high interactions with the support (*i.e.* $MoO_3/\gamma\text{-}Al_2O_3 \rightarrow MoO_2/\gamma\text{-}Al_2O_3$), and iii) a large peak from 625 °C to 975 °C, characteristic of the reduction of $NiAl_2O_4$. Compared to 10Ni sample, this last peak is shifted towards lower temperatures ($\Delta T$ = - 50 °C). The better reduction of nickel oxide caused by addition of molybdenum has been notably described by Brito *et al.* [31]. The authors highlighted that when calcined at low temperatures (400-600 °C), NiO and $MoO_x$ oxides supported on $\gamma$-$Al_2O_3$ were accelerating the reduction of each other phase. Youn *et al.* [32] explained this phenomenon by the formation of a Ni-$MoO_x$ phase preventing Ni to form $NiAl_2O_4$ spinel, which is difficult to reduce. Furthermore, the X-Ray pattern obtained after TPR measurement (Figure 1b, Table 2) shows an important shift of the Ni (2 0 0) diffraction ray towards the Mo (2 0 0) ray, which indicates the possible presence of a Ni-Mo alloy ($Ni_{0.90}Mo_{0.10}$).

The TPR profile of 10Ni-2Mn sample (Figure 1a) presents two reduction peaks located at 400 °C and 575 °C, which are respectively attributed to the $MnO_2 \rightarrow Mn_2O_3$ and $Mn_2O \rightarrow MnO$ reduction steps. This sample shows a slight shift of the nickel oxide reduction step towards lower temperatures ($\Delta T$ = - 20 °C) compared to 10Ni sample. Indeed, it is also asserted that Ni-$MnO_x$ interactions prevent the formation of hardly reducible $NiAl_2O_4$ spinel, which consequently favor the reduction of Ni [33]. Nevertheless, the X-Ray pattern after TPR measurement of 10Ni-2Mn sample do not evidence the formation of any Ni-Mn alloy.

The TPR profile of 10Ni-2Cu sample (Figure 1a) shows at first a broad peak with low intensity located between 300 °C and 500 °C, which is attributed to the reduction of copper oxides in $Cu^{(0)}$ metallic nanoparticles. For this sample, the reduction step of $NiAl_2O_4$ is significantly shifted towards lower temperatures ($\Delta T$ = - 60 °C). This enhancement of the Ni reducibility due to Cu addition is well-known in the literature [34,35]. It is attributed to the early presence of metallic copper nanoparticles, which favors the adsorption and activation of $H_2$ molecules by spillover effect [36]. The formation of $Ni_{0.76}Cu_{0.24}$ alloy is suggested on the X-Ray pattern by the absence of $Cu^{(0)}$ rays and by the shift of the Ni (2 0 0) ray towards the diffraction angle of $Cu^{(0)}$ (2 0 0) (Figure 1b, Table 2). Indeed, by their similar crystalline organization and their close atomic radius, Ni and Cu are known to easily form homogeneous solid solutions [34,35,37]. Furthermore, from both X-Ray and TEM measurements (Figure 2c), a noticeable decrease of the size of the metallic Ni-Cu particles after TPR measurement is observed (*i.e.* for 10Ni-2Cu sample: $d_{TEM}$ = 16 nm and $d_{XRD}$ = 15 nm; whereas for 10Ni sample:

$d_{TEM}$ = 30 nm and $d_{XRD}$ = 23 nm) (Table 2). The presence of smaller Ni-Cu particles by addition of Cu is apparently characteristic [34].

The TPR profile of 10Ni-2Co sample (Figure 1a) presents two peaks around 400 °C and 550 °C, which are respectively attributed to the reduction of cobalt oxides with low and high interactions with the alumina support. The addition of Co broadened the reduction step of Ni and shifted the reduction peak of Ni towards higher temperatures ($\Delta T$ = + 100 °C) compared to 10Ni sample. This delay of the Ni reduction caused by Co has also been noticed by Sengupta *et al.* [38]. Furthermore, Bortolozzi *et al.* [39] highlighted by Raman spectroscopy that the addition of a small amount of Co to $Ni/Al_2O_3$ materials could lead to the formation of a stable Ni(Co)O solid solution, thus increasing the reduction temperature of Ni. In Figure 1b, the shift of the Ni (2 0 0) ray towards lower diffraction angles observed in the X-Ray pattern suggests the presence of $Ni_{0.75}Co_{0.25}$ alloy after TPR measurement (Table 2).

The TPR profile of 10Ni-Fe sample (Figure 1a) presents a small reduction peak located at 450 °C, attributed to the $Fe_2O_3 \rightarrow Fe_3O_4$ reduction step, and a broad $H_2$ consumption peak, from 500 °C to 1000 °C, attributed to the further reduction of iron oxide species with different interactions with the alumina support. Noteworthy, the reduction step of the $NiAl_2O_4$ phase of this sample is shifted towards higher temperatures ($\Delta T$ = + 75 °C). Indeed, the iron oxide species being reduced at higher temperatures, it is asserted that strong $Ni/Fe_yO_x$ interactions led to a harder reducibility of the nickel oxides [16,40]. Furthermore, the presence of $Ni_{0.82}Fe_{0.18}$ alloy after TPR measurement is evidenced by the shift of the Ni (2 0 0) diffraction ray in the X-Ray pattern (Figure 1b, Table 2). Indeed, Ni and Fe easily form solid solutions [13,16,40]. The absence of an alteration of the $\gamma$-$Al_2O_3$ phase confirms that instead of interacting with the support, the Fe species in 10Ni-2Fe sample are more inclined to form strong interactions with Ni.

### 3.1.3. Catalytic activity

The catalytic performances of all 10 wt. % Ni/$\gamma$-$Al_2O_3$ catalysts doped with 2 wt. % of metal were measured. Figures 3a and 3b show the toluene conversion, $C_T$, as a function of time and the toluene reforming rate, $r_T$, as a function of the amount of carbon deposit. Figures 3c and 3d show the benzene selectivity, $S_B$, and the methane conversion, $C_{CH4}$. The metallic particle size, the nature of the metallic phases present after the catalytic test as well as the catalytic performances of the samples are presented in Table 3. Figure 4 shows the DSC curves performed on samples after catalytic tests.

From the results, it appears that the doping of the catalysts with copper leads to the worst results. Indeed, 10Ni-2Cu sample shows a low $r_T$ value (3.9 .$10^{-2}$ $mol_{Tolu}/(g_{Ni}.h)$), a low $C_{CH4}$ value (4 %), and the largest amount of carbon deposit (0.13 $g_{Carbon}/g_{Cata}$) (Table 3). However, the TG-DSC curve (Figure 4) and TEM observations (not shown here) show that the carbon deposit of this sample is exclusively constituted of amorphous carbon. It could be explained by the formation of a Ni-Cu alloy phase confirmed by XRD after test (Table 3). Indeed, it is known that the dissolution of carbon inside a Ni-Cu alloy is more difficult than inside pure Ni particles, which consequently results in the prevention of filamentous carbon formation [41]. However, whereas in the case of methane reforming, the spacing of Ni atoms by Cu atoms prevents the formation of C-C bonds and reduces the amount of carbon deposit by “ensemble control” [41,42], this phenomenon do not seem to be relevant in the case of the reforming of toluene. Hence, the progressive deactivation of 10Ni-2Cu sample throughout the test (Figure 3a) is assumed to be caused by the formation of a high amount of amorphous carbon, which covers and deactivates the surface of the Ni-Cu particles. Finally, the low $CH_4$ value observed for 10Ni-2Cu sample (Table 3, Figure 3c-d) could be correlated to the work of Kratzer *et al.* [43], which showed by DFT calculations, that the activation energy of methane chemisorption on a nickel atom in the Ni (1 1 1) surface is significantly smaller if the neighbor atom is an atom of Cu instead of Ni.

The catalysts doped with iron (*i.e.* 10Ni-2Fe sample) or with cobalt (*i.e.* 10Ni-2Co sample) show similar trends. Indeed, their $C_T$ and $C_{CH4}$ values are lower (Figure 3a, Table 3) compared to 10Ni sample, which could be caused by an insufficient reduction of the metallic active sites (see TPR curves, Figure 1). Both samples are more inclined to form filamentous carbon (Figure 4, Table 3). These observations could explain why Co/Fe elements are commonly used to modify Ni-based catalysts in order to produce carbon nanotubes at industrial scale [44–46].

In the case of manganese addition (*i.e.* 10Ni-2Mn sample), the catalyst shows lower $C_T$ and $C_{CH4}$ values compared to 10Ni sample (Figures 3a and 3d, Table 3), but this is balanced by a very low amount of carbon deposit (0.05 $g_{Carbon}/g_{Cata}$). DSC curves (Figure 4) and TEM observations (not shown) reveal that the carbon deposit of this sample is only constituted of amorphous carbon. These results are in accordance with the literature and are attributed to the migration of the $MnO_x$ species to the surface of the metallic nickel particles [33,47–49]. By their location at the surface of the metallic nickel particles, the $MnO_x$ species could partially decrease the catalytic activity because of the blockage of active sites. However, they could provide high anti-coking effects. Indeed, it has been asserted that the moderate basicity of the manganese oxide species improves the adsorption of the $H_2O$ and $CO_2$ molecules [49] and that the redox properties of the $MnO_x$ species favor their dissociation and the migration of the $O^*$ species [33,47,49]. This higher rate of formation of oxidative species led to a better oxidation of the intermediate compounds and of the carbonaceous deposits, which explained the low $S_B$ value and the low carbon deposit obtained for 10Ni-2Mn sample. Furthermore, in the case of methane reforming, Seok *at al.* [49] suggested that the covering of the particle by $MnO_x$ species divided the surface of $Ni^{(0)}$ particle into different patches, which were large enough to perform the $CH_4$ reforming, but too small to allow the formation of carbon deposit thanks to "ensemble control" effect [41,42].

The catalysts doped with 2 wt. % of molybdenum show the more interesting results. Indeed, 10Ni-2Mo sample shows a higher $r_T$ and a relatively good $C_{CH4}$ value (7 %) for an acceptable amount of carbon deposit (*Coke* = 0.11 $g_{Carbon}/g_{Cata}$) compared to 10Ni sample (Figures 3a and 3d, Table 3). Similarly to Mn, the $MoO_x$ species are also known to be able to surround and cover the $Ni^{(0)}$ particles of the catalyst. These $MoO_x$ species are generally in different oxidation states ($Mo^{n+}$ with $4 < n < 6$) [50], which is believed to increase the redox cycles of the Ni-$MoO_x$ compounds and to favor the dissociation reactions of $H_2O$ and of $CO_2$ [14,32,51]. Moreover, Maluf *et al.* [52] also obtained higher methane reforming activity for $Ni/Al_2O_3$ materials doped with Mo. Since the authors observed that the addition of Mo decreased the surface metallic area, but increased the specific activity of the active sites, they concluded that the higher reforming activity was caused by a transfer of electrons from the $MoO_x$ species to the nickel atoms, leading to an increase of the electron density of the Ni atoms. Though the influence of $MoO_x$ species is relatively well detailed, there is a lack of literature about the effect of the formation of Ni-Mo alloys.

### *3.2. Catalysts doped with two different metals*

10 wt. % Ni/$\gamma$-$Al_2O_3$ catalysts doped with 2 wt. % of one metal and 2 wt. % of a second metal (Metal = Cu, Co, Mn, Mo or Fe) were synthesized, characterized, and tested for the reforming of 24,000 ppmv of toluene at 650 °C. Figure 5 gives an overview of the catalytic properties (*i.e.* $r_T$, $S_B$, and $C_{CH4}$) for all samples.

It appears that the samples 10Ni-2Co-2Mo and 10Ni-2Mn-Mo show the best catalytic performances. Hence, the properties and catalytic performances of both catalysts are presented in the following parts.

### 3.2.1. Composition, crystallinity, particle size and reducibility of samples doped with Co+Mo or Mn+Mo

It is shown in Table 1 that, for samples 10Ni-2Co-2Mo and 10Ni-2Mn-2Mo, the theoretical and actual compositions are similar. Figure 6 shows the TPR profiles and the post-TPR X-Ray patterns of 10Ni-2Co-2Mo and 10Ni-2Mn-2Mo samples. For a better comparison, the results of 10Ni, 10Ni-2Mn, 10Ni-2Mo, and 10Ni-2Co samples are also added to the graphs. Table 2 shows the metallic particle sizes and their compositions after TPR determined by TEM and XRD measurements.

10Ni-2Co-2Mo sample shows a broad $H_2$ consumption peak located between 400 °C and 700 °C attributed to the reduction of Co and Mo oxide species (Figure 6a). Whereas the Ni reduction step of 10Ni-Co sample is shifted towards higher temperatures ($\Delta T$ = + 100 °C, Figure 6a) and the reduction step of Ni of 10Ni-2Mo sample is shifted towards lower temperatures ($\Delta T$ = - 50 °C, Figure 6a), for 10Ni-2Co-2Mo sample, the reduction step of Ni is only slightly shifted towards lower temperatures ($\Delta T_{Ni}$ = - 15 °C, Figure 6a). This observation indicates that during their reduction step, the Ni oxide species are influenced by both Co and Mo. The analysis of the X-Ray patterns after TPR measurements suggests the presence of a $Ni_{0.91}Mo_{0.09}$ phase, but no Ni-Co phase is visible (Figure 6b and Table 2).

The reduction profile of 10Ni-2Mn-2Mo sample (Figure 6a) shows a simultaneous reduction of the $MnO_x$ and $MoO_x$ species, located respectively at 425 °C and 550 °C. 10Ni-2Mn-2Mo sample also shows a shift of the reduction step of nickel towards lower temperatures ($\Delta T$ = - 50 °C) similar to the one observed for 10Ni-2Mo sample (Figure 6a). The analysis of the X-Ray pattern after TPR measurements suggests the presence of a $Ni_{0.9}Mo_{0.1}$ alloy (Figure 6b and Table 2). The association of Mn and Mo apparently allows decreasing the sintering of the metallic particles since 10Ni-2Mn-2Mo sample shows low $d_{\mathrm{XRD}}$, $d_{\mathrm{TEM}}$ (21 and 25 nm respectively), and $\sigma_{\mathrm{TEM}}$ (5 nm) values (Table 2).

### 3.2.2. Catalytic performances of samples doped with Co+Mo or Mn+Mo

Figure 7 shows the toluene conversion, $C_{\mathrm{T}}$, as a function of time and the toluene reforming rate, $r_{\mathrm{T}}$, as a function of the amount of carbon deposit for 10Ni-2Co-2Mo and 10Ni-2Mn-2Mo samples, the simple doped catalysts (*i.e.* 10Ni-2Co, 10Ni-2Mo, and 10Ni-2Mn sample), and 10Ni sample. Figure 8 shows the DSC curves after catalytic tests. The metallic particle sizes, the type of metallic phase present after catalytic tests, and the catalytic performances of the samples are presented in Table 3.

The high $r_{\mathrm{T}}$ value ($8.4 .10^{-2}$ $\mathrm{mol_{Tolu}/(g_{Ni}.h)}$) observed for 10Ni-2Co-2Mo sample compared to 10Ni-2Co sample, and the presence of a Ni-Mo alloy after test (Table 3) indicates that the activity of this sample is mostly attributed to the addition of Mo. However, whereas 10Ni-2Co and 10Ni-2Mo samples present high $S_{\mathrm{B}}$ values (13-17 %, Table 3), 10Ni-2Co-2Mo sample in contrary presents a lower $S_{\mathrm{B}}$ value (8 %, Table 3). The observation of the post-test DSC curve of 10Ni-2Co-2Mo sample in Figure 8 also reveals a synergistic effect between Co and Mo. Indeed, whereas 10Ni-2Mo and 10Ni-2Co samples present both amorphous and filamentous carbon deposits (Figure 4), the carbon deposit of 10Ni-2Co-2Mo sample is in contrary entirely constituted of amorphous type. Furthermore, for similar or even higher $r_{\mathrm{T}}$ values, 10Ni-2Co-2Mo sample presents lower amount of coke after test (0.08 $\mathrm{g_{Carbon}/g_{Cata}}$, Table 3) compared to 10Ni-2Co and 10Ni-2Mo samples (respectively 0.10 $\mathrm{g_{Carbon}/g_{Cata}}$ and 0.11 $\mathrm{g_{Carbon}/g_{Cata}}$, Table 3).

In the case of 10Ni-2Mn-2Mo sample, the high $r_{\mathrm{T}}$ value ($7.1 .10^{-2}$ $\mathrm{mol_{Tolu}/(g_{Ni}.h)}$) and the possible presence of a Ni-Mo alloy after test (Table 3) also indicates that the activity of the samples is mostly attributed to the addition of Mo. Moreover, the combination of Mn and Mo allows avoiding in this case the formation of filamentous carbon (Figure 8) and to decrease the formation of carbon for 10Ni-2Mn-2Mo sample (*Coke* = 0.08 $g_{Carbon}/g_{Cata}$).

### *3.3. Influence of higher loading*

In view of the results obtained in the upper parts of this work, it was decided to study 10 wt. % Ni/$\gamma$-$Al_2O_3$ catalysts doped with a higher loading (*i.e.* 4 wt. %) of Mn or Mo as second metal. Table 1 shows the theoretical and actual compositions of these samples.

#### 3.3.1. Crystallinity, particle size, and reducibility of 10 wt. % Ni/$\gamma$-$Al_2O_3$ catalysts doped with 4 wt. % of Mn or Mo

Figure 9 shows the influence of Mo and Mn loadings (*i.e.* 0, 2 or 4 wt. %) on the reduction of 10 wt. % Ni/$\gamma$-$Al_2O_3$ catalysts. The metallic particle sizes and compositions after TPR measurements determined by XRD and TEM analyses are presented in Table 2.

It is observed in Figure 9 that the increase of Mn content from 2 wt. % to 4 wt. % do not have strong consequence on the reduction of the sample. Furthermore, similarly as for 10Ni-2Mn sample, the X-Ray pattern after TPR measurement do not allow confirming the formation of any Ni-Mn alloy or revealing the presence of $MnAl_2O_x$ phases for 10Ni-4Mn sample.

The increase of the loading of Mo up to 4 wt. % lead to a catalyst with a similar reducibility as 10Ni-2Mo sample (Figure 9a), but which presents a Ni-Mo alloy richer in Mo ($Ni_{0.83}Mo_{0.17}$) and with smaller metallic nanoparticles after TPR measurement ($d_{TEM}$ = 22 nm, $\sigma_{TEM}$ = 7 nm, and $d_{XRD}$ = 17 nm, Table 2). This observation is in accordance with the literature and confirms the fact that $MoO_x$ species plays the role of barrier for preventing the growth of $Ni^{(0)}$ particles [14,32].

### 3.3.2. Catalytic performances of 10 wt. % Ni/γ-$Al_2O_3$ catalysts doped with 4 wt. % of Mn or Mo

Figures 10 shows the toluene conversion, $C_T$, as a function of time and the toluene reforming rate, $r_T$, as a function of the carbon deposit for the samples prepared with different loadings of Mo or Mn. Figure 11 shows the DSC curves performed on samples after catalytic test. The metallic particle sizes and compositions after test determined by TEM and XRD measurements as well as the catalytic performances are listed in Table 3.

The increase of the loading of Mo up to 4 wt. % decreases the catalytic activity. Indeed, 10Ni-4Mo sample presents a lower $r_T$ value (5.9 .$10^{-2}$ $mol_{Tolu}/(g_{Ni}.h)$), a higher $S_B$ value (21 %), and a lower $C_{CH4}$ value (5 %) compared to 10Ni-2Mo sample (Table 3). This is attributed to a large covering of the surface of the $Ni^{(0)}$ particles by $MoO_x$ species, which in high amounts are known to block the sites necessary for the reforming reactions [14,52]. Furthermore, in Figure 10, the progressive activation of the catalyst is slower and no steady conversion value is reached after 300 min. Since the TPR measurement of the sample do not evidence a delay of the Ni reduction, it is also assumed that the high covering of the Ni particles by $MoO_x$ species prevents the reduction , as it is observed in previous works [14,32]. Nevertheless, in accordance with the literature, this high covering is highly efficient to protect 10Ni-4Mo sample from coking (*Coke* = 0.03 $g_{Carbon}/g_{Cata}$) and from the formation of filamentous carbon (Figure 11).

The catalytic performance of the 10 wt. % Ni/γ-$Al_2O_3$ catalyst doped with a higher loading of Mn (10Ni-4Mn sample) is affected in a similar way as for the Mo doping. This is also assumed to be caused by a large covering of the $Ni^{(0)}$ particles by $MnO_x$ species [33,47–49]. Indeed, it could be observed in Table 3 that 10Ni-4Mn sample also presents a lower $r_T$ value and difficulties to be activated during the catalytic test. Furthermore, 10Ni-4Mn sample also presents a remarkably low amount of carbon deposit after test (0.03 $g_{Carbon}/g_{Cata}$), which is only constituted of amorphous carbon (Figure 11).

Hence, it appears that despite their low catalytic activity, the samples doped with 4 wt. % of either Mo or Mn might be appropriated for long-term tests at 650 °C thanks to their remarkable anti-coking performances.

## 4. Conclusions

In this work, the influence of metallic dopant addition in 10 wt. % Ni/$\gamma$-$Al_2O_3$ catalysts was studied in terms of physico-chemical properties and catalytic activity. Seventeen doped Ni/$\gamma$-$Al_2O_3$ catalysts were synthesized by the sol-gel process. One Ni/$\gamma$-$Al_2O_3$ catalyst without dopant and one sample of pure $\gamma$-$Al_2O_3$ were also synthesized as reference material.

The vast screening performed in this work allowed determining which elements were the most interesting for the doping of 10 wt. % Ni/$\gamma$-$Al_2O_3$ catalysts.

It appeared that Ni/$\gamma$-$Al_2O_3$ catalysts doped with 2 wt. % of copper showed the worst catalytic performances. Indeed, the sample showed a progressive deactivation during the catalytic tests caused by the formation of a large amount of amorphous carbon. As the formation of Ni-Cu alloys was suggested by XRD measurement, and that the samples presented a high benzene selectivity, it was assumed that the deactivation by coking was caused by a lower ability of the Ni-Cu alloy to break aromatic rings. However, the presence of a Ni-Cu alloy prevented the dissolution of C atoms inside the metallic particles and avoided the formation of filamentous carbon.

The addition of Co or Fe caused a more difficult reduction of Ni because of strong interactions between Ni-$FeO_x$ and Ni(O)Co species, which led to low catalytic activity values during catalytic tests performed at 650 °C. Co or Fe favored the production of filamentous carbon.

Though they showed slightly lower activities, all Ni/$\gamma$-$Al_2O_3$ catalysts doped with 2 wt. % of Mn showed interesting anti-coking properties and no formation of filamentous carbon during the catalytic tests at 650 °C. The beneficial influence of the addition of Mn was attributed to the good ability of the $MnO_x$ species to increase the adsorption-dissociation of $H_2O$ and $CO_2$ molecules, which led to a better gasification of the carbonaceous deposits at the surface of the $Ni^{(0)}$ particles. A higher loading of Mn (*i.e.* 4 wt. %) prevented an efficient activation of Ni during the catalytic test, probably due to a large covering of $Ni^{(0)}$ particles by $MnO_x$ species. Despite its low activity, the sample doped with 4 wt. % of Mn presented a remarkably low amount of carbon deposit after a test at 650 °C.

Molybdenum proved to be the most interesting metal dopant. Indeed, when tested at 650 °C, the Ni/$\gamma$-$Al_2O_3$ catalyst doped with 2 wt. % of Mo showed the highest toluene reforming activity, for an acceptable amount of carbon deposit. This better activity was attributed to: i) a more efficient reduction of Ni evidenced by TPR measurement; ii) an increase in the adsorption-dissociation of $H_2O$ and $CO_2$ molecules by the $MoO_x$ species; iii) an increase in the oxygen ionic conductivity of Ni caused by electronic interactions between Mo and Ni, which increased the gasification rate of the $CH_x$ species to CO and $H_2$. A higher amount of Mo (*i.e.* 4 wt. %) decreased the catalytic activity during the standard test at 650 °C, probably because of a large covering of $Ni^{(0)}$ particles by $MoO_x$. However, in that case, this sample presented a very low amount of carbon deposit after test.

Among all 10 wt. % Ni/$\gamma$-$Al_2O_3$ catalysts doped with 2 wt. % of two different metals, the samples which combined Mn+Mo or Co+Mo showed the most interesting catalytic performances at 650 °C. Both samples showed high toluene reforming activity and low amounts of carbon deposit.

For equal loadings, it seems more advantageous from a catalytic activity and catalyst lifetime point of view, to dope the catalysts with two types of elements (*i.e.* 2 X 2 wt. % of metals), than with only type of element (*i.e.* 4 wt. % of metal).

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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: Composition and textural properties of samples**

| **Sample** | **Theoretical composition (wt. %)** | **Actual composition (wt. %)** | **$S_{BET}$ ($m^2/g$)** | **$V_p$ ($cm^3/g$)** | **$V_{DR}$ ($cm^3/g$)** |
|---|---|---|---|---|---|
| 10Ni | 90.0 $Al_2O_3$ / 10.0 Ni | 90.5 $Al_2O_3$ / 9.5 Ni | 240 | 0.3 | 0.08 |
| 10Ni-2Mo | 88.0 $Al_2O_3$ / 10.0 Ni / 2.0 Mo | 89.1 $Al_2O_3$ / 9.0 Ni / 1.9 Mo | 240 | 0.3 | 0.08 |
| 10Ni-2Mn | 88.0 $Al_2O_3$ / 10.0 Ni / 2.0 Mn | 89.6 $Al_2O_3$ / 9.7 Ni / 1.8 Mn | 260 | 0.3 | 0.09 |
| 10Ni-2Cu | 88.0 $Al_2O_3$ / 10.0 Ni / 2.0 Cu | 89.4 $Al_2O_3$ / 9.3 Ni / 2.3 Cu | 255 | 0.3 | 0.08 |
| 10Ni-2Co | 88.0 $Al_2O_3$ / 10.0 Ni / 2.0 Co | 88.4 $Al_2O_3$ / 9.7 Ni / 1.9 Co | 240 | 0.3 | 0.08 |
| 10Ni-2Fe | 88.0 $Al_2O_3$/ 10.0 Ni / 2.0 Fe | 88.0 $Al_2O_3$/ 9.6 Ni / 2.4 Fe | 235 | 0.3 | 0.08 |
| 10Ni-2Mn-2Mo | 86.0 $Al_2O_3$ / 10.0 Ni / 2.0 Mn / 2.0 Mo | 85.3 $Al_2O_3$ / 10.9 Ni / 1.7 Mn / 2.1 Mo | 245 | 0.3 | 0.08 |
| 10Ni-2Co-2Mo | 86.0 $Al_2O_3$ / 10.0 Ni / 2.0 Co / 2.0 Mo | 86.0 $Al_2O_3$ / 10.2 Ni / 1.8 Co / 2.0 Mo | 250 | 0.3 | 0.08 |
| 10Ni-4Mo | 86.0 $Al_2O_3$ / 10.0 Ni / 4.0 Mo | 86.0 $Al_2O_3$ / 10.0 Ni / 4.0 Mo | 235 | 0.3 | 0.08 |
| 10Ni-4Mn | 86.0 $Al_2O_3$ / 10.0 Ni / 4.0 Mn | 86.0 $Al_2O_3$ / 10.0 Ni / 4.0 Mn | 240 | 0.3 | 0.08 |

$S_{BET}$: specific surface area determined from nitrogen adsorption-desorption isotherms and using the Brunauer-Emmet-Teller theory; $V_p$: porous volume determined from nitrogen adsorption-desorption isotherms at saturation pressure; $V_{DR}$: microporous volume determined from Dubinin-Raduskevitch theory.

**Table 2: Metallic particles sizes and X-Ray observations after TPR measurements for all catalysts.**

| Sample | Particle sizes | | | Ni-Metal (2 0 0) ray (°) | Reference (2 0 0) ray of pure doping metal (°) | Possible phases |
|---|---|---|---|---|---|---|
| | $d_{TEM}$ (nm) | $\sigma_{TEM}$ (nm) | $d_{XRD}$ (nm) | | | |
| 10Ni | 30 | 9 | 23 | 51.83 | Ni = 51.83 | - |
| 10Ni-2Mo | 28 | 7 | 20 | 51.11 | Mo = 44.95 | Possibility of $Ni_{0.90}Mo_{0.10}$ alloy / No ray of molybdenum oxide or $Mo^{(0)}$ visible |
| 10Ni-2Mn | 27 | 8 | 23 | 51.80 | Mn = 52.38 | No ray of manganese oxide visible |
| 10Ni-2Cu | 16 | 4 | 15 | 51.56 | Cu = 50.43 | Possibility of $Ni_{0.76}Cu_{0.24}$ alloy / No ray of $Cu^{(0)}$ visible |
| 10Ni-2Co | 35 | 10 | 26 | 51.76 | Co = 51.59 | Possibility of $Ni_{0.75}Co_{0.25}$ alloy / No ray of cobalt oxide visible |
| 10Ni-2Fe | 29 | 9 | 23 | 51.53 | Fe = 50.52 | Possibility of $Ni_{0.82}Fe_{0.18}$ alloy / No ray of iron oxide or $Fe^{(0)}$ visible |
| 10Ni-2Mn-2Mo | 25 | 5 | 21 | 51.11 | Mo = 44.95<br>Mn = 52.38 | Possibility of $Ni_{0.9}Mo_{0.1}$ phase |
| 10Ni-2Co-2Mo | 41 | 9 | 25 | 51.30 | Co = 51.59<br>Mo = 44.95 | Possibility of $Ni_{0.91}Mo_{0.09}$ phase |
| 10Ni-4Mo | 22 | 7 | 17 | 50.73 | Mo = 44.95 | Possibility of $Ni_{0.83}Mo_{0.17}$ alloy / No ray of molybdenum oxide or $Mo^{(0)}$ visible |
| 10Ni-4Mn | 26 | 8 | 21 | 51.80 | Mn = 52.38 | No ray of manganese oxide visible |

$d_{TEM}$: metallic particle size median measured by TEM; ; $\sigma_{TEM}$ : standard deviation associated to TEM measurements; $d_{XRD}$: metallic nickel crystallite size obtained by XRD.

**Table 3: Metallic particles sizes, metal alloy phases and catalytic performances for all catalyst. Test conditions: 650 °C, 300 min, 24.000 ppmv of toluene, *GHSV* of 5000 h$^{-1}$.**

| | Particle sizes | | | Possible metal phase | Catalytic performances | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|
| **Sample** | $d_{TEM}$ (nm) | $\sigma_{TEM}$ (nm) | $d_{XRD}$ (nm) | | $C_T$ (%) | $r_t$ (mol$_{Tolu}$ /(g$_{Ni}$.h)) | $S_B$ (%) | $C_{CH4}$ (%) | *Coke* (g$_{Carbon}$/ g$_{Cata}$) ±0.01 | **Filamentous carbon** |
| 10Ni | 12 | 4 | 12 | Ni | 51 | 6.7 .10$^{-2}$ | 15 | 10 | 0.10 | No |
| 10Ni-2Mo | 12 | 6 | 11 | $Ni_{0.97}Mo_{0.03}$ | 54 | 8.5 .10$^{-2}$ | 13 | 7 | 0.11 | No |
| 10Ni-2Mn | 10 | 2 | 14 | Ni | 35 | 4.4 .10$^{-2}$ | 9 | 2 | 0.05 | No |
| 10Ni-2Cu | 8 | 4 | 8 | $Ni_{0.75}Cu_{0.25}$ | 31 | 3.9 .10$^{-2}$ | 16 | 4 | 0.13 | No |
| 10Ni-2Co | 15 | 11 | 13 | $Ni_{0.8}Co_{0.2}$ | 31 | 3.7 .10$^{-2}$ | 17 | 5 | 0.10 | + |
| 10Ni-2Fe | 14 | 5 | 17 | $Ni_{0.82}Fe_{0.18}$ | 30 | 3.7 .10$^{-2}$ | 12 | 7 | 0.08 | + |
| 10Ni-2Mn-2Mo | 11 | 3 | 11 | $Ni_{0.97}Mo_{0.03}$ | 54 | 7.1 .10$^{-2}$ | 7 | 10 | 0.08 | No |
| 10Ni-2Co-2Mo | 12 | 4 | 11 | $Ni_{0.97}Mo_{0.03}$<br>$Ni_{0.2}Co_{0.8}$ | 58 | 8.4 .10$^{-2}$ | 8 | 9 | 0.08 | No |
| 10Ni-4Mo | 13 | 7 | 14 | $Ni_{0.97}Mo_{0.03}$ | 43 | 5.9 .10$^{-2}$ | 5 | 21 | 0.03 | No |
| 10Ni-4Mn | 12 | 4 | 15 | Ni | 29 | 3.4 .10$^{-2}$ | 5 | 9 | 0.03 | No |

$d_{TEM}$: metallic particle size median measured by TEM; ; $\sigma_{TEM}$ : standard deviation associated to TEM measurements; $d_{XRD}$: metallic nickel crystallite size 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.