



## HYDROGEN PRODUCTION BY LOW TEMPERATURE METHANE STEAM REFORMING USING Ag AND Au MODIFIED ALUMINA SUPPORTED NICKEL CATALYSTS

Mihaela D. LAZAR,\* Monica DAN, Maria MIHET, Valer ALMASAN,  
Vasile REDNIC and George BORODI

National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath Street,  
400293 Cluj-Napoca, Roumania

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Au (1%) and Ag (1%) modified Ni (8%) catalysts deposited on  $\gamma$ -alumina were prepared by co-impregnation method. The catalysts structure was investigated by  $N_2$  adsorption – desorption, XRD and XPS techniques revealing the presence of Au and Ag on the catalyst's surface and their interaction with nickel and alumina. The catalysts were tested in methane steam reforming reaction for hydrogen production in a fixed bed flow reactor, at temperature ranged from 450°C to 700°C and  $CH_4/H_2O$  ratio of 1/4. At low reaction temperatures ( $T < 600^\circ C$ ) the addition of Au improves the catalytic activity and stability of Ni catalyst. The addition of Ag decreases the catalytic properties of Ni/ $Al_2O_3$ . At high temperatures the gold influence is not so important, and the catalysts deactivate.

### INTRODUCTION

The hydrogen production gains more and more attention in the last period, hydrogen being a very attractive energy vector and an alternative energy source, due to the low pollution in its utilization and due to the predictable finishing of fossil fuels in the near future. The main disadvantage is that hydrogen cannot be found in nature as pure, gaseous compound and by now the costs for its production, storage and distribution remain very high. Classic catalytic methane reforming uses supported nickel catalysts and requires high temperatures and pressures in order to obtain good catalytic activity.<sup>1</sup> It is known that one of the biggest problems of nickel catalysts in methane steam reforming is the catalysts deactivation occurred by carbon deposition and/or catalysts oxidation. One solution to improve the catalyst's performance is to selectively change the surface structure through the formation of a superficial alloy.<sup>2</sup> Noble metals, such as Ag and Au, added to Ni/oxide have been tested and have shown promising results

for coke minimization in the steam reforming of hydrocarbons.<sup>3,4</sup> In this paper we report the preparation, characterization and testing of two modified alumina supported nickel catalyst designed to lower the reaction temperature and to increase the catalyst's stability. The new catalysts were prepared by adding gold, respectively silver to nickel. They were tested for hydrogen production by methane steam reforming at temperatures starting with 450°C and atmospheric pressure.

### RESULTS AND DISCUSSION

#### Catalysts characterization

The  $N_2$  adsorption – desorption isotherms of all three studied catalysts are of type IV which corresponds to mesoporous solids (Fig. 1). The pore size distribution is relatively narrow and uniform with a medium diameter of 50 Å (Fig. 1b).

\* Corresponding author: [diana.lazar@itim-cj.ro](mailto:diana.lazar@itim-cj.ro)

The total surface area and pores total volume of prepared catalysts are not influenced very much by the addition of the secondary metal, but in all cases, are smaller than the values recorded for alumina support. The mesoporous structure of these materials is catalytically favorable and contributes to good catalytic activity and stability by dispersing the metal nanoparticles and assuring a good access of reagents to catalytic active sites.

The XRD patterns of the as prepared catalysts contain three major peaks attributed to Ni: Ni(1 1 1) at  $44.5^\circ$ ; Ni(2 0 0) at  $51.8^\circ$  and Ni(2 2 0) at  $76.5^\circ$  (Fig. 2). There is no evidence of NiO (expected to appear at  $37.3^\circ$  and  $43.3^\circ$ )<sup>5</sup> in the XRD patterns of the studied samples indicating that all the oxide was reduced during catalyst preparation and nickel is present on the support only in the metallic form.

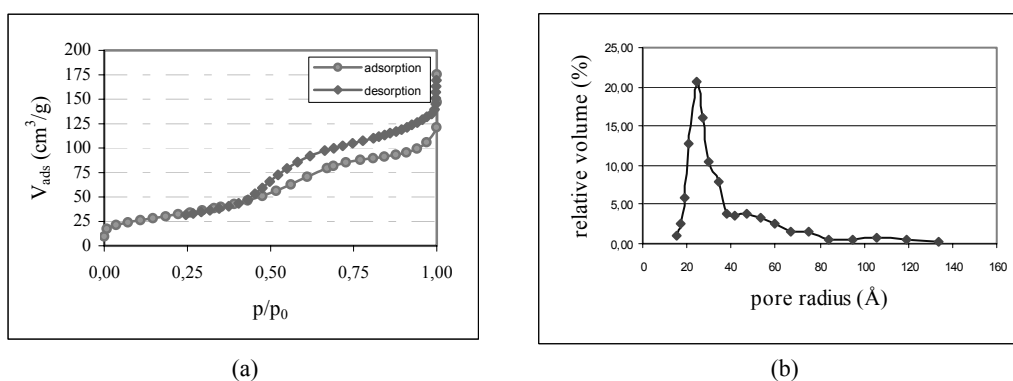


Fig. 1 – (a) N<sub>2</sub> adsorption – desorption isotherms of Ni–Au/Al<sub>2</sub>O<sub>3</sub> (b) Pore size distribution for Ni–Ag/Al<sub>2</sub>O<sub>3</sub>.

Table 1

Total surface area, pores volumes and radius and medium Ni crystallite size for modified nickel catalysts

Parameter	Catalyst			
	Al <sub>2</sub> O <sub>3</sub>	Ni/Al <sub>2</sub> O <sub>3</sub>	Ni-Au/Al <sub>2</sub> O <sub>3</sub>	Ni-Ag/Al <sub>2</sub> O <sub>3</sub>
S <sub>t</sub> (m <sup>2</sup> /g)	134	108	111	105
V <sub>p</sub> (cm <sup>3</sup> /g)	0.21	0.18	0.18	0.17
R <sub>m</sub> (Å)	25	25	25	25
D <sub>mNi</sub> (Å)	-	85,6	86,9	72,7

S<sub>t</sub> – total surface area; V<sub>p</sub> – pores total volume; R<sub>m</sub> – pores medium radius; D<sub>mNi</sub> – the size of nickel particles deposited on alumina

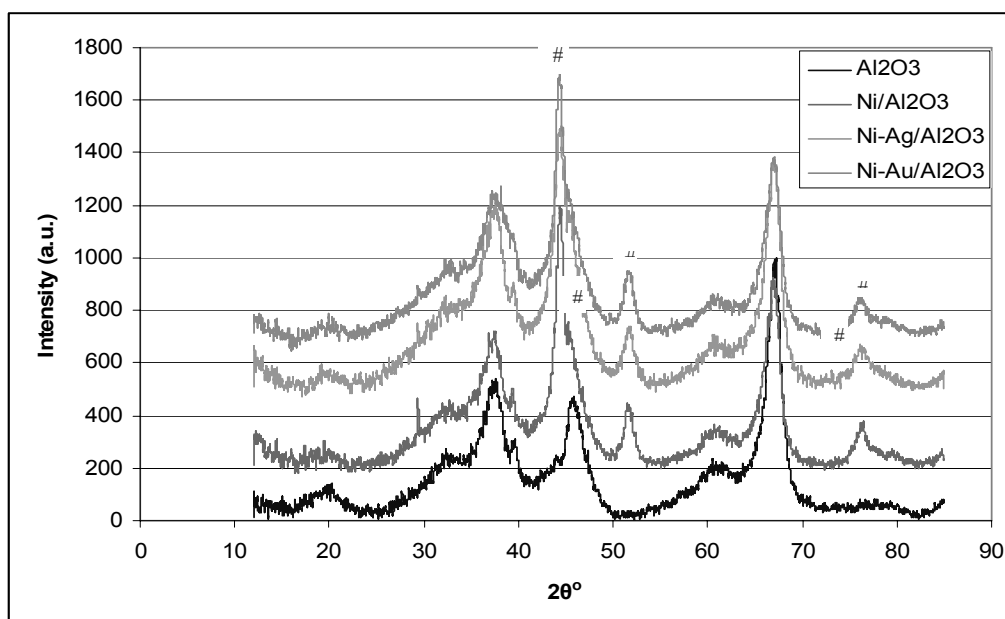


Fig. 2 – XRD patterns of the modified alumina supported nickel catalysts; (#) - peaks correspond to Ni.

The Au and Ag diffraction lines are not visible in the XRD patterns, due to the small concentration of these metals on the catalyst surface. The Ni crystallite sizes were determined from X-ray spectra using the Scherrer equation (Table 1). The addition of gold to the nickel catalysts does not change the nickel crystallite size. The silver addition in turn, produces smaller nickel nanoparticles.

XPS spectroscopy was used to study the elements which are present on the catalysts surface and their oxidation states. In all samples, excepted gold containing catalyst, nickel appears in XPS spectra in three forms: one corresponds to metallic Ni and has the main line of Ni 2p<sub>3/2</sub> level at 852.3 eV and two forms correspond to ionic nickel (Ni<sup>2+</sup>), with binding energy of about 855.1 eV and about 857.2 eV. For gold containing sample only two forms of nickel are present: a metallic form at 853,3 eV and ionic nickel Ni<sup>2+</sup> at 857,7 eV.<sup>6</sup> The peak from 852,3 eV corresponds to a form of metallic nickel which, though are deposited on the support surface is little influenced by it. The presence of ionic nickel on catalysts surface is due to superficial NiO (the peak at 855.1 eV) and to some nickel aluminate entities (857.2 eV). It seems that

the cleaning procedure used in XPS experiments to remove the surface impurities was not totally efficient, and some of the superficial nickel oxide formed on the Ni nanoparticles surface in the catalyst pasivation step, is still present on the surface. This oxide is totally removed before catalytic activity experiments (in activation step), so in working conditions the catalysts is expected to contain only metallic nickel. XRD measurements evidenced only Ni in metallic state. The ionic nickel, evidenced in XPS spectra, cannot be observed by XRD measurements because these methods determine the crystalline structure in bulk states while XPS gives information mainly from the surface of the investigated samples. This confirms that the ionic nickel states are present only on the surface of the crystallites.

Both noble metals – gold and silver – added to the Ni/Al<sub>2</sub>O<sub>3</sub> are present on the catalyst surface as proved by the XPS spectra of metal modified nickel catalysts sample. Au 4f<sub>7/2</sub> peak is centered on 84 eV and Ag 3d<sub>5/2</sub> on 368.2 eV (Fig. 3).<sup>6</sup> These values of binding energy show that both Au and Ag are only in the metallic form on the catalyst surface.

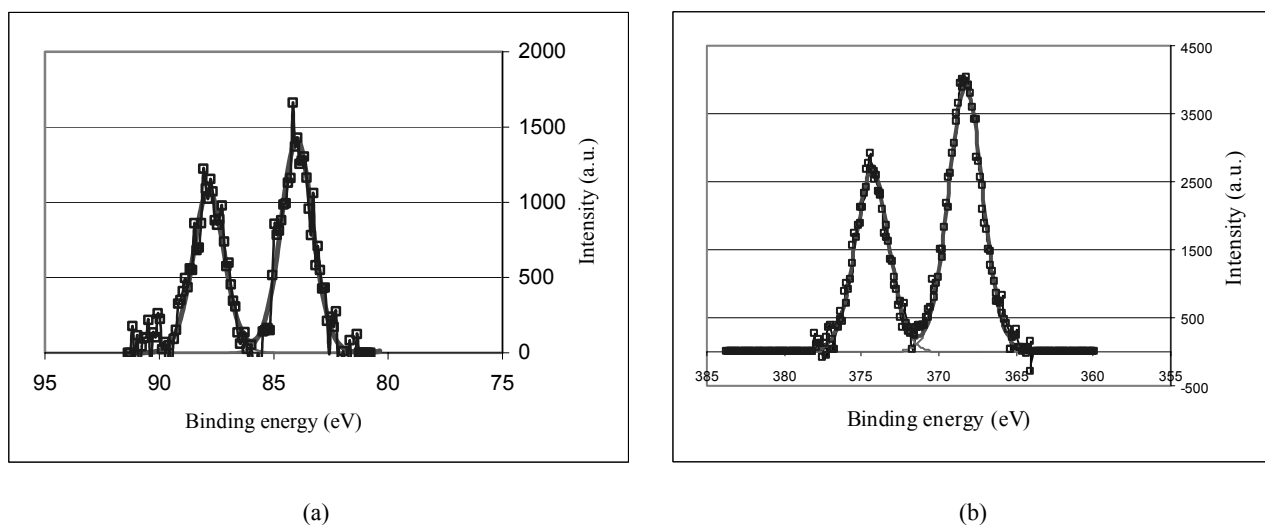
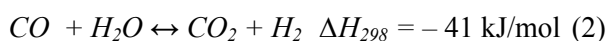
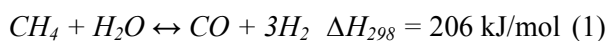


Fig. 3 – XPS spectra of Au 4f<sub>7/2</sub> and 4f<sub>5/2</sub> (a) and Ag 3d<sub>5/2</sub> and 3d<sub>3/2</sub>.

### Catalytic activity results

The alumina supported nickel catalysts modified by addition of Au or Ag were tested for methane steam reforming in the temperature range of 450 – 700°C. The methane flow was 35 ml/min and methane to steam ratio (C/S) was 1:4. The main reactions which take place are:



The main products of the steam reforming reaction (MSR) (1) are H<sub>2</sub> and CO. Although carbon monoxide is transformed in carbon dioxide in water gas-shift reaction (WGS) (2), it is still present in the reaction products mixture in low concentrations, especially at high reaction temperatures. Fig. 4 shows the data of catalytic activity for the unmodified and modified Ni catalysts expressed as maximum methane conversion versus reaction temperature.

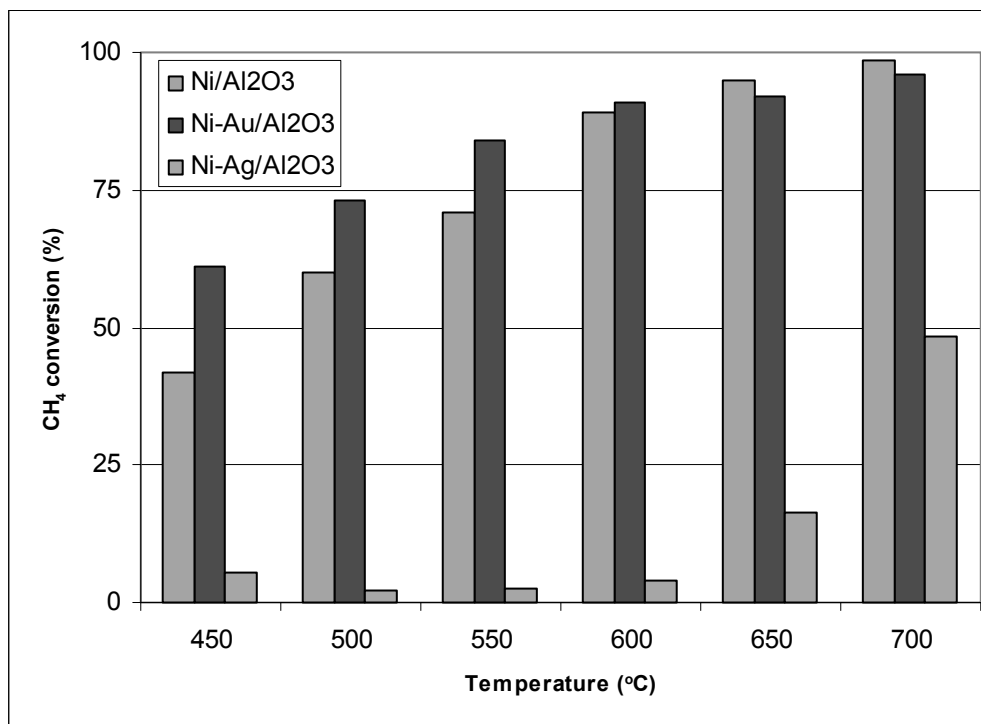


Fig. 4 – Methane conversion over the Au and Ag modified alumina supported Ni catalysts versus reaction temperature.

The methane conversion increases with the reaction temperature for the all studied catalysts. At temperatures lower than 600°C the addition of 1% of Au to the Ni catalysts improves the catalysts performances. The methane conversion is higher with about 20% at 450°C and about 15% at 550°C for Ni-Au bimetallic catalysts compared with Ni/Al<sub>2</sub>O<sub>3</sub>. At temperatures higher than 600°C the methane conversion has similar values for Au modified and unmodified nickel catalysts, indicating a similar catalytic activity. The explanation of gold effect on Ni catalytic properties is based on the previous studies which show that at temperatures lower than 500°C, gold is present on supported Ni-Au/MgAl<sub>2</sub>O<sub>4</sub> catalysts as nanoparticles dispersed rather on the nickel surface than on the oxide.<sup>4</sup> A superficial Au-Ni alloy is formed at the gold – nickel interface, and the catalysts exhibiting this type of alloy are active for butane steam reforming and more stable to deactivation than the unpromoted Ni catalysts.<sup>7</sup> These studies revealed that gold atoms or clusters are localized mainly on the low coordinated Ni atoms situated on steps and corners, which also represent the most active catalytic sites for methane adsorption and dissociation. Due to this reason, in the previous mentioned papers, hydrocarbon conversion on Au-Ni catalysts was

similar, or even lower than the conversion obtained with simple Ni catalyst. Our Ni-Au/Al catalyst presents a better catalytic activity for MSR at low temperatures than Ni/Al. The explanation must take into account that in our experiments the catalyst composition, support nature and reaction conditions (C/S ratio, and flows) were different and seem to assure better conditions for MSR reaction. On the other hand, gold catalysts are known to be active for WGS reaction at low temperatures. The blockage of nickel active sites by gold is compensated by the possible formation of new centers for WGS on gold and/or Au-Ni alloy, where the CO species adsorbed on the Ni sites neighboring Au atoms are oxidized. The enhancement of WGS reaction, by continuously removing CO, contributes to the enhancement of the MSR reaction. At higher temperatures, there is evidence of gold dissolution into the bulk nickel.<sup>8</sup> The disappearance of well organized gold nanoparticles from the catalyst surface, as a result of Au atoms diffusion into the bulk Ni, and/or reorganizing of Au atoms into bigger, less active, nanoparticles, explains the lack of any effect of gold addition to Ni/Al<sub>2</sub>O<sub>3</sub> catalysts at temperatures higher than 600°C.

The addition of Ag to the Ni/Al<sub>2</sub>O<sub>3</sub> drastically decreases the catalytic properties of the nickel

catalysts. At low temperatures, the methane conversion has very low values (less than 10%) and starts to increase at temperatures higher than 600°C. The maximum methane conversion is registered for the reaction carried out at 700°C and is about 50%. This result is in correlation with literature data<sup>3</sup> which report that 0.3 wt.% and 0.6 wt.% Ag promoted Ni (15 wt.%) catalysts exhibit a strong decrease of methane conversion at 600°C compared to unpromoted nickel catalyst. The decrease of conversion is compensated by an increase of catalyst stability toward deactivation by carbon formation. This behavior was explained by a preferential blockage of low coordinated Ni atoms by Ag, but also by a modification of the superficial nickel structures of the high coordination sites (like terraces). These types of modifications are dependent on the Ag concentration. In our case, the addition of 1 wt.% of Ag to the 6 wt.% of Ni deposited on alumina, proved to be a too high silver concentration in order to obtain a functional catalyst at low temperatures.

The catalysts stability against deactivation was studied by determining the methane conversion after 48h of reaction. The results are presented in Table 2 for two reaction temperatures: 500°C and 700°C.

At low reaction temperature – 500°C – the conversion of the Au modified catalysts show significant stability after 48 h, and no deactivation was observed during this reaction time. An

improving of Ni catalysts stability by Au addition was previously reported for *n*-butane steam reforming<sup>4,9</sup> and is due to blockage by added gold, of nickel most active sites, which are responsible for carbon formation and also the property of gold to easily oxidize the chemisorbed carbon atoms. For unmodified Ni catalysts the catalytic activity start to decrease after 4h on stream and a slow, long time deactivation occurs. This deactivation is most probably due to carbon deposition on Ni catalytic active sites. The Ag modified Ni catalyst practically doesn't work at this reaction temperature probably due to the cover of Ni by the Ag atoms. At high reaction temperatures – 700°C – the unmodified Ni catalyst present better stability than Ni-Au, no deactivation being observed after 48h. The Ni-Au catalyst starts to deactivate after first hour on stream, suggesting that the properties of catalytic active sites starts to change immediately after reaction starts. The deactivation is most probably due to: (i) sintering of gold nanoparticles, which is known to occur at high temperatures<sup>9</sup>, followed by the destruction of active sites situated on gold, and also to (ii) migration of gold over the nickel, and blocking of some Ni active sites, due to the mobility of the gold nanoparticles on the catalyst surface at high temperatures. A strong catalyst deactivation occurs on Ni-Ag catalysts, showing that in our working conditions the addition of silver does not improve the stability of nickel catalysts.

Table 2

Maximum methane conversion and conversion after 48h for methane steam reforming catalyzed by Ni, Ni-Au and Ni-Ag catalysts

Catalysts	Temperature (°C)	Maximum conversion <sup>(a)</sup> (%)	Final conversion <sup>(b)</sup> (%)
Ni/Al <sub>2</sub> O <sub>3</sub>	500	73	65
Ni – Au/Al <sub>2</sub> O <sub>3</sub>		84	84
Ni – Ag/Al <sub>2</sub> O <sub>3</sub>		3	0
Ni/Al <sub>2</sub> O <sub>3</sub>	700	99	98
Ni – Au/Al <sub>2</sub> O <sub>3</sub>		96	85
Ni – Ag/Al <sub>2</sub> O <sub>3</sub>		49	12

(a) – conversion after 1 h; (b) – conversion after 48h; reaction conditions: CH<sub>4</sub>: H<sub>2</sub>O = 1:4, carrier gas Ar, total flow = 50 ml/min

## EXPERIMENTAL

Supported Ni catalysts (8 wt.% Ni) modified with Ag (1 wt.%) and Au (1 wt.%) were prepared by co-impregnation of  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> (Alpha Aesar) with aqueous solutions of Ni(NO<sub>3</sub>)<sub>2</sub> × 6H<sub>2</sub>O and AgNO<sub>3</sub> for Ni-Ag/Al<sub>2</sub>O<sub>3</sub>, and Ni(NO<sub>3</sub>)<sub>2</sub> × 6H<sub>2</sub>O and HAuCl<sub>4</sub> × 3H<sub>2</sub>O for Ni-Au/Al<sub>2</sub>O<sub>3</sub>, respectively. The reagents were purchased from Merck and used without other modifications. The impregnated samples were dried at room temperature overnight, calcined under argon at 400°C for 4h, and reduced in H<sub>2</sub> at 400°C

for 4h. After reduction the catalysts were pasivated in a N<sub>2</sub> flow which contains traces of O<sub>2</sub>.

Total surface area (S<sub>t</sub>), pore volume (V<sub>p</sub>) and pore radius (R<sub>m</sub>) of the samples were obtained from N<sub>2</sub> adsorption-desorption isotherms, using the BET model for S<sub>t</sub> determination, and Dollimore-Heal method for V<sub>p</sub> and R<sub>m</sub>. The isotherms were measured using a Sorptomatic 1990 apparatus.

The XRD analyses were made using a Bruker D8 advanced diffractometer with Cu K $\alpha$ 1 radiation, operation voltage 40 kV and current 40mA. The average sizes of Ni crystallite were determined using Scherrer's equation.

The XPS spectra were recorded using a Specs spectrometer with non-monochromatized Al K $\alpha$  radiation at room temperature. The pressure in the ultra-high vacuum chamber was in the 10<sup>-10</sup> mbar range during the measurements. The spectra were recorded after the surface was cleaned by sputtering with Ar ions.

The catalytic activity measurements for methane steam reforming took place in a laboratory device composed by feed section, reactor, and analytical unit. The gaseous components and the water enter in the vaporizer using a liquid pump and mass flow controllers, respectively. The carrier gas is Ar, the total flow was 50 mL/min, and the C/S ratio was 1:4. The reactions were carried out under atmospheric pressure using catalyst powders (1 g; granulation 80 – 100  $\mu$ m) diluted with alumina powder (1 g) of similar granulometry. The reaction temperature ranged from 450°C to 700°C. Prior reaction, the catalysts samples were activated at 400°C in H<sub>2</sub> flow at 30 ml/min for 2h. Effluent gases composition was analyzed by gas chromatography, using two columns and TCD detector.

Methane conversion was calculated using the formula:

$$C_{CH_4} = \frac{[CH_4]_{in} - [CH_4]_{out}}{[CH_4]_{in}} \times 100 \quad (3)$$

where [CH<sub>4</sub>]<sub>in</sub> and [CH<sub>4</sub>]<sub>out</sub> are the methane concentrations in the inlet and outlet gaseous mixture, respectively.

## CONCLUSIONS

A series of bimetallic alumina supported nickel catalysts were prepared, characterized and tested for hydrogen production by methane steam reforming at low temperatures. The catalysts were prepared by co-impregnation of alumina support with Au (or Ag) and nickel, resulting in three catalysts: Ni/Al<sub>2</sub>O<sub>3</sub>, Ni–Ag/Al<sub>2</sub>O<sub>3</sub>, Ni–Au/Al<sub>2</sub>O<sub>3</sub>. The catalysts were characterized using nitrogen adsorption – desorption, TPR and XRD techniques. All catalysts were tested in methane steam reforming reaction at temperatures ranged from 450°C to 750°C. Ni–Au bimetallic catalysts showed a better catalytic activity and stability at

low temperatures (under 600°C) than the simple Ni/Al<sub>2</sub>O<sub>3</sub> catalyst. The addition of Ag proved to decrease all the catalytic properties of Ni/Al<sub>2</sub>O<sub>3</sub>. Future experiments using different concentration of metals and different reaction conditions will allow us to obtain a catalyst with improved qualities for methane steam reforming at low temperatures.

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