Babeş-Bolyai University, Faculty of Chemistry and Chemical Engineering

PhD Thesis
Summary

Multicomponent heterogeneous catalysts for H_2 production from renewable sources

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INTRODUCTION

After the energy crisis in the 1970s considerable attention was conferred on the development of alternate energy sources. The energy demand of the world is increasing exponentially; therefore in the future we can expect a decrease in the reserve of the fossil fuels. Another important aspect that has to be taken into consideration is that the combustion of fossil fuels has serious negative effects on environment because of carbon dioxide (CO_2) emission.

Through the research community, hydrogen is considered a very attractive energy vector. It is clean with no CO_2 emissions and its combustion generates an important amount of energy and does not result in any emission other than water vapor, having a low impact on the environment.

Nowadays the trend is to find clean energy sources, biomass representing a very interesting raw material. The ethanol obtained from biomass is an attractive feedstock in terms of hydrogen content, non toxicity, transport, storage and handling. The process of steam reforming involves a series of reaction in order to produce hydrogen, some of them being favored by the catalytic material and reaction conditions used.

The main objectives of this research were (1) to design and develop high performance catalysts that are capable of efficiently catalyzing the production of hydrogen in the steam reforming process, (2) evaluation of the newly prepared catalysts in ethanol steam reforming process, (3) evaluation of the newly prepared catalysts in bio-ethanol steam reforming process.

The catalysts investigated are Ni based catalysts on different supports such as aluminium oxide and zirconium oxide. Characterization studies by different techniques would be carried out for the fresh and spent catalysts to correlate their activities with different physical and chemical properties. Additionally we have tried to highlight those catalysts that show the best performance in terms of maximizing the catalytic parameters (ethanol conversion, acetic acid conversion, hydrogen selectivity, stability of the catalyst) investigated.

The evaluation of the catalysts is performed in optimal reaction conditions so that the values of the investigated catalytic parameters are as high as possible.

The thesis is structured in five chapters.

The first chapter presents a scientific literature review relating to renewable raw materials and of the technologies used to produce hydrogen. A detail description is also provided of the catalysts cited in the literature that are used in the ethanol catalytic reforming process.

In **chapter II** are described in detail the methods used for the preparation of mono and bimetallic catalysts tested in this study. Also a detailed description of the physico-chemical methods is presented for a more complete characterization of the prepared catalysts. Catalysts characterisation was performed in order to obtain the relationship between the catalyst characteristic and its performance.

In **chapter III and IV** are presented the catalytic performances of the prepared catalyst, which are being assessed in process of steam reforming of ethanol in chapter III, namely bio-ethanol in chapter IV.

The optimum performance evaluation of the prepared catalyst has been possible through various changes of process parameters: temperature, gas flow and liquid flow. The stability of the catalyst would be tested by time-on-stream runs. The investigated catalytic parameters are: ethanol conversion, acetic acid conversion, hydrogen yield or hydrogen production and stability of catalyst.

The thesis concludes with a chapter in which are presented the conclusions of the results obtained in the previous chapters. Most of the results presented in this thesis have been published in scientific journals and at international and national conferences.

<u>Note: chapter numbering, tables, figures, and the paragraph is that of a PhD thesis.</u>

Keywords: metallic catalysts, renewable feedstock’s (ethanol, bio-ethanol), catalytically steam reforming, aluminium oxide, zirconium oxide

ORIGINAL RESEARCH

Phd THESIS OBJECTIVS

The overall objective of this thesis is to develop a high performance catalyst capable to transform ethanol/bio-ethanol in hydrogen via catalytic steam reforming process.

In order to achieve these important goals various phases of research were mapped out, each phase having a set of objectives.

- Eleven different catalyst were prepared through different methods impregnation, co-impregnation, successive impregnation and precipitation
- Characterization of the fresh prepared catalyst in ordered to correlate the catalyst characteristic and its performance. The characterization technique used are: Inductively coupled plasma mass spectrometry (ICP-MS), X-ray diffraction (XRD), temperature programmed reduction (TPR), temperature programmed desorption (TPD), temperature programmed oxidation (TPO), thermo-gravimetric analysis (TGA).
- The evaluation of the catalyst was carried out in a fixed bed reactor in order to screen the catalysts and to identify the one who present the best catalytic performances from the eleven prepared catalysts
- Catalyst evaluation was performed in ethanol/ bio-ethanol steam reforming process through various changes of process parameters like temperature (150-350°), gas flow (10-300 ml/min) and liquid flow (0.1-0.6 ml/min)
- Catalyst evaluation was carried out in ethanol/ bio-ethanol steam reforming process through various changes of the basic catalyst (Ni/Al): by supplementary addition of another metal (Cu, Ag and Au), by modifying the catalyst support through the addition of another oxide (La_2O_3 and CeO_2) to alumina or zirconia support and by variation of the metallic content deposed on the catalyst support (1%-3% Cu).

CHAPTER II.

CATALYST PREPARATION AND CHARACTERISATION

2. Catalyst preparation

We have prepared a Ni/Al_2O_3 catalyst designated as Ni/Al being considered as basic catalyst. This catalyst has been modified by addition of a supplementary metal, or by addition of oxides to the catalyst support or by complete modification of the support, obtaining thus new catalyst. A detail description of the newly prepared catalyst and their composition can be found in Table 2.1.

Table 2.1 The composition and preparation method of the catalysts

Catalyst	Catalyst abreviation	Support	Added metal		Added oxide	Preparation method
Ni/Al_2O_3	Ni/Al	Al_2O_3	Ni	-	-	Impregnation
Ni-Cu/Al_2O_3	Ni-Cu(1)/Al Ni-Cu(2)/Al Ni-Cu(3)/Al		Ni	Cu(1%, 2%, 3%)	-	Co-impregnation
Ni-Au/Al_2O_3	Ni-Au/Al		Ni	Au	-	Co-impregnation
Ni-Ag/Al_2O_3	Ni-Ag/Al		Ni	Ag	-	Co-impregnation
Ni/La_2O_3-Al_2O_3	Ni/La-Al		Ni	-	La_2O_3	Successive impregnation
Ni/CeO_2 -Al_2O_3	Ni/Ce-Al		Ni	-	CeO_2	Successive impregnation
Ni/ZrO_2	Ni/Zr	ZrO_2	Ni	-	-	Precipitation, impregnation
Ni/La_2O_3-ZrO_2	Ni/La-Zr		Ni	-	La_2O_3	Precipitation, Successive impregnation
Ni $/CeO_2$ -ZrO_2	Ni/Ce-Zr		Ni	-	CeO_2	Precipitation, Successive impregnation

2.4. Catalyst characterization

2.4.1. Inductively coupled plasma mass spectrometry (ICP-MS)

The metal content of the prepared catalyst was determined using ELAN DCR-e (Perkin Elmer Inc., USA) apparatus. The analysis consists in bringing the metal from the catalyst surface to a solution by treating 0.1g of fresh catalyst with 5 ml HNO_3, for catalyst containing Ni, Cu and Ag. For gold containing catalysts we use 5 ml of “aqua regia”. The obtained results are presented in Table 2.2.

Table 2.2. The obtained values through ICP- MS analysis: C_{Ni}- Ni concentration and C_{Au} , C_{Ag}, C_{Cu} – Au, Ag and Cu concentration

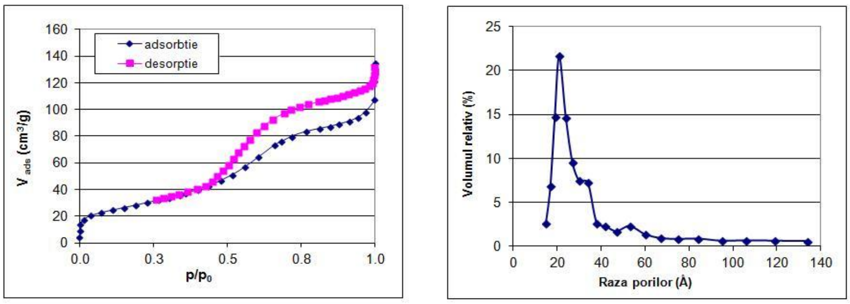
Catalyst	**C_{Ni}**	**C_{Ag}**	**C_{Au}**	**C_{Cu}**
Ni/Al	6.8	-	-	-
Ni/Zr	8	-	-	-
Ni/La-Al	6.7	-	-	-
Ni/La-Zr	7.8	-	-	-
Ni/Ce-Al	7	-	-	-
Ni/Ce-Zr	7.1	-	-	-
Ni-Ag/Al	6	0.9	-	-
Ni/Au-Al	6.8	-	1	-
Ni-Cu(1)/Al	6.1	-	-	0.8
Ni-Cu(2)/Al	7.1	-	-	1.7
Ni-Cu(3)/Al	6.2	-	-	2.8

2.4.2. Surface area, pore volume and pore radius determination by volumetric technique

Catalyst surface area determination is very important due to fact that in heterogeneous catalysis the main reactions involved are on the surface of the catalysts. The measurements were determined with a Sorptomatic 1990 (Thermo-Scientific, USA) using the N_2 adsorption at liquid nitrogen temperature. The adsorption isotherms and the pore distribution are represented in Figure 2.1.

For the Ni based catalyst on alumina support, the addition of the supplementary metal and oxide, does not seem to have an important influence on the surface area, pore volume and on pore dimensions.

The catalyst on zirconium oxide support present a lower surface area, a lower porosity compared with alumina supported catalyst. This means that the pore volume is lower but the pore radius is higher.



(a) (b)

Figure 2.1 Adsorption- desorption isotherm (a) and pore volume distribution (b) for Ni/Al catalyst

Table 2.3. The characteristics of the Ni based catalyst: S_{tot}-total surface area, S_{Ni}-metallic surface area, V_p-pore volume, R_m-pore radius, $D_{Ni\text{-}XRD}$-crystallite dimensions

Catalyst	**S_{tot} (m^2/g)**	**S_{Ni} (m^2/g)**	**V_p (cm^2/g)**	**R_m (Å)**	**$D_{Ni\text{-}XRD}$ (nm)**
Ni/Al	102	2.4	0.18	25	10
Ni-Au/Al	109	2.2	0.18	25	8.7
Ni-Ag/Al	105	1.2	0.17	26	7.2
Ni/La-Al	100	6.3	0.15	25	6.7
Ni/Ce-Al	99	4.5	0.14	25	7.6
Ni-Cu(1)/Al	104	1.3	0.18	23	5.9
Ni-Cu(2)/Al	105	1.12	0.17	24	8.1
Ni-Cu(3)/Al	109	1	0.18	24	12.5
Ni/Zr	52.5	1	0.06	60	57.4
Ni/La-Zr	50.7	5.5	0.08	125	29
Ni/Ce-Zr	59	4.6	0.1	135	35.4

2.4.3. X-ray diffraction (XRD)

The wavelength of X rays are of Å order being capable to penetrate solids, this technique can be used to determine the internal structure of materials, crystallite dimensions, structural defects and micro tensions in the elementary cell. Using a Brucker D8 with a $CuK_{\alpha}1$ source we were able to record the XRD spectra of the fresh catalyst. The spectra were recorded from 20° to 80° with a step of 0.01°/s. Ni crystallite dimensions were calculated using Scherrer's equation.

In the recorded spectra, for all the catalysts on alumina support, lines are present which are attributed to Ni situated at 44.5°, 51.8° and 76.5° (Figure 2.3 and Figure 2.4(a, b)). For Ni/Ce-Al besides the lines corresponding to Ni, we observe 4 additional peaks attributed to CeO_2 at 28.6°, 33°, 47.3° and 56.7°. The lines corresponding to La_2O_3 are not present, indicating or high dispersion or that the oxide is present in an amorphous state.

The catalyst on ZrO_2 support present the same peaks corresponding to Ni previously identified. For the catalyst modified with cerium oxide and lanthanum oxide we were not able to identify the peaks corresponding to these oxides, probably due to very high dispersion on the catalyst surface.

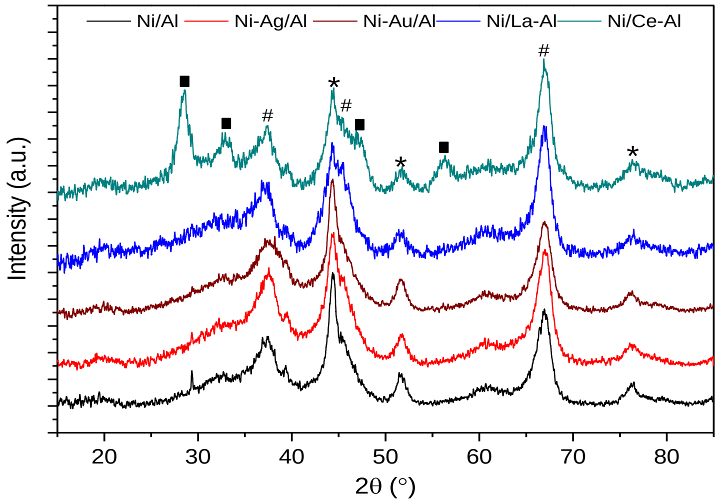


Figure 2.3 XRD spectra for alumina based catalysts, where: # -Al_2O_3, *- Ni, ■ -CeO_2

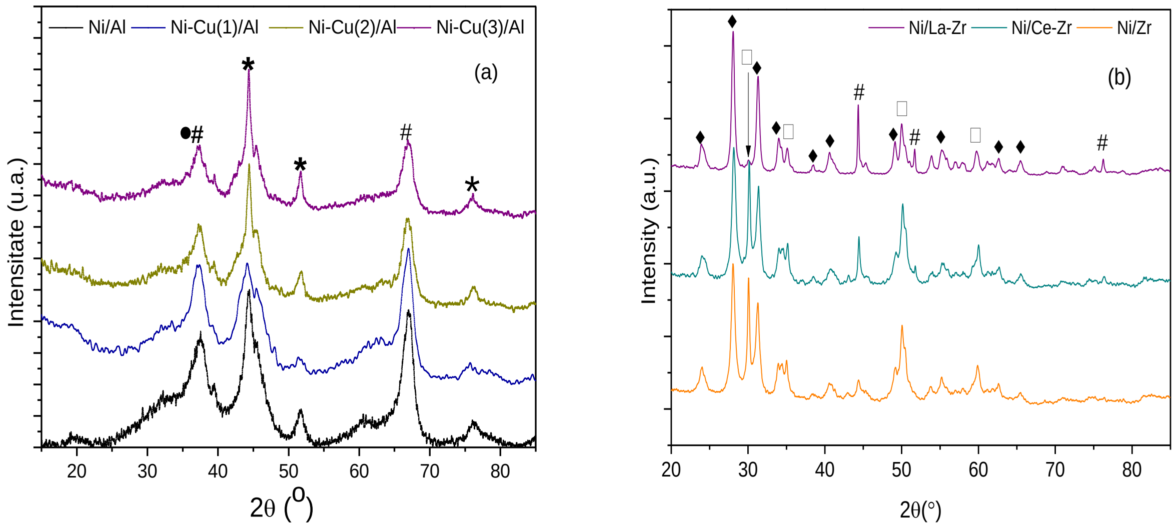


Figure 2.4 a, b. XRD spectra for fresh prepared catalysts , where: # -Al_2O_3, *- Ni, •- $CuAl_2O_4$, ■ - CeO_2, ♦ - monoclinic ZrO_2, □- tetragonal ZrO_2.

2.4.4. Temperature programmed reduction (TPR)

This technique of analysis is very useful in order to investigate the nature and the strength of the interaction between the oxides of the active metal and the support for the catalytic precursors. The reduction profile of every catalytic precursor was recorded using a TPRO 1100 (Thermo Scinetific, USA) (Figure 2.5).

The addition of the noble metals (Ag, Au, and Cu) to Ni/Al has the effect of lowering the temperature of main reduction peak. The recorded TPR profile for Ni/Ce-Al catalyst is not so different compared to the TPR profile recorded for Ni/Al. The addition of the La_2O_3 to the Ni/Al has the effect of lowering the main reduction peak and also a change in peak intensity (Figure 2.6).

The addition of the cerium and lanthanum oxide to the zirconium oxide support has effect of raising the temperature of the main reduction peak. This change in the reduction temperature is more probably dued to the different type of interactions between NiO with the La-Zr and Ce-Zr support compared to the one of NiO with ZrO_2.

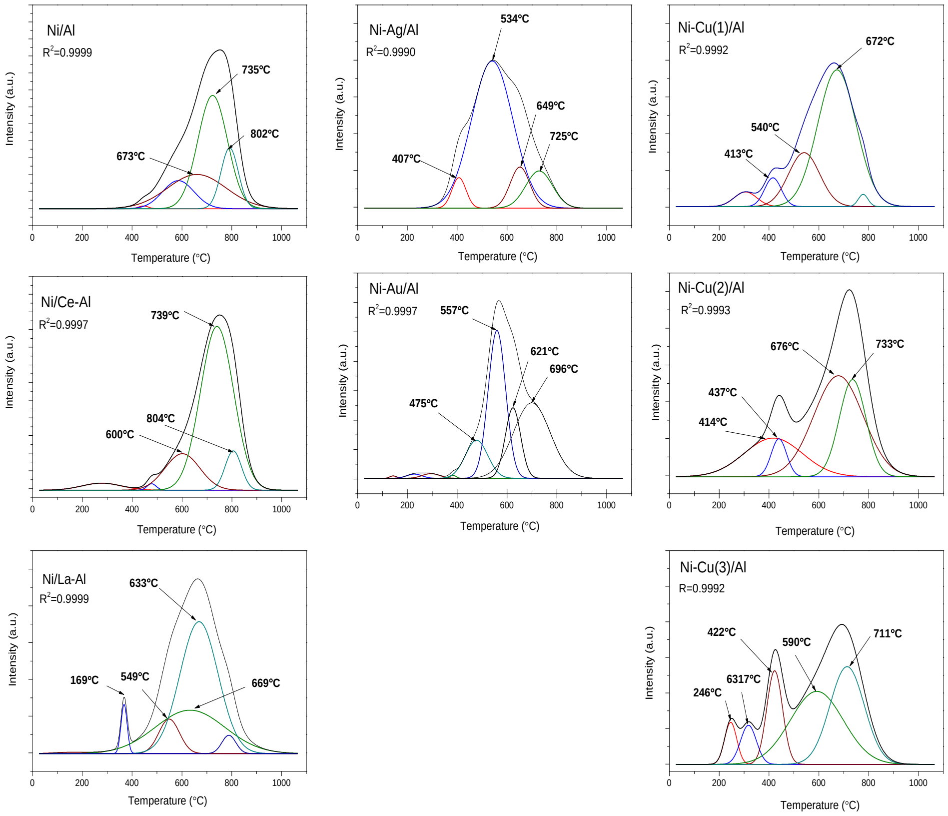


Figure 2.5 Reduction profile the Ni alumina supported catalyst

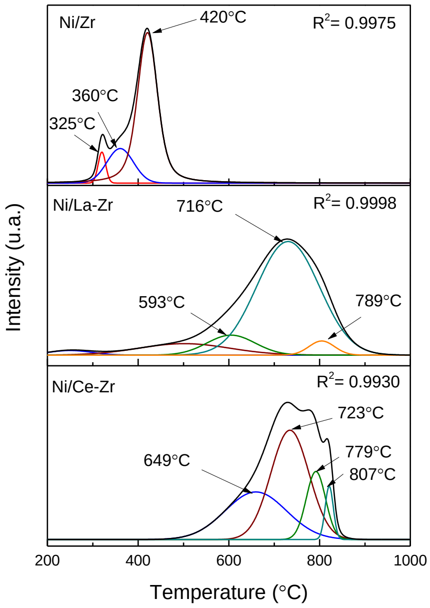


Figure 2.7. Reduction profile the Ni zirconium supported catalyst

2.4.5. Temperature programmed desorption (TPD)

For the heterogeneous catalyst we have the possibility through TPD analysis to investigate the type and distribution of the catalytic active sites from the catalyst surface.

In the recorded TPD profiles for all the tested catalyst we observe two domains of H_2 desorption peaks: one situated at lower temperature < 500°C referred as type I peaks and one situated at higher temperatures >500° C denoted as type II peaks. The type 1 peaks are generally attributed to hydrogen desorbed form Ni nanoparticles and in direct correlation with the number of catalytic active sites. The type II peaks are attributed to hydrogen originally located on subsurface layers and/or to the support.

For the catalyst with supplementary metal (Au, Ag and Cu) on alumina support (Figure 2.9), we observe that the majority of the identified peaks are of type II peaks. Apparently there is no modification in the recorded TPD profile while raising the copper content on the catalyst surface (Figure 2.10).

For the catalyst with added oxide to alumina support, we observe a clear distinction between the two temperature domains (Figure 2.11). The addition of CeO_2 to the alumina support does not seem to influence greatly the peak distribution. In comparison the addition of La_2O_3 to Ni/Al has the effect of modifying the peak distribution, so that the quantity of hydrogen originated from temperature domain I is higher.

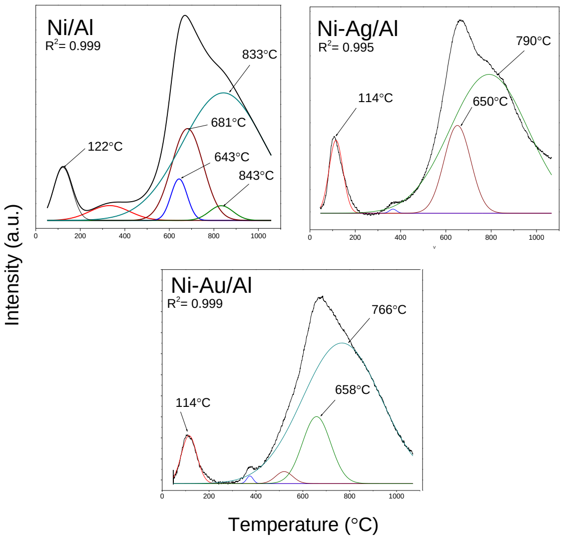


Figure 2.9 TPD recorded profiles and their deconvolution for catalyst with Au and Ag on alumina support

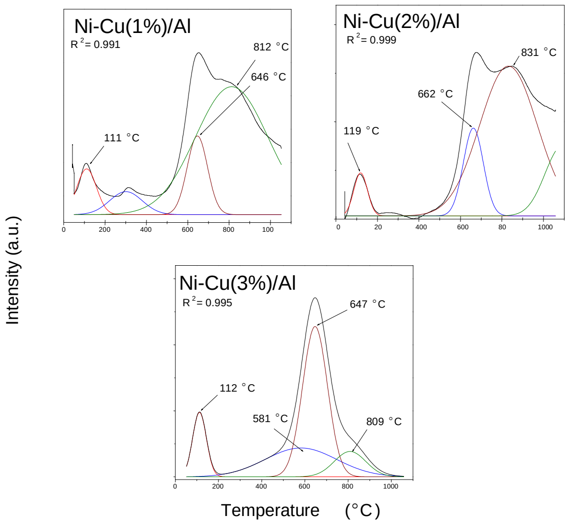


Figure 2.10. TPD recorded profiles and their deconvolution for catalyst with Cu on alumina support

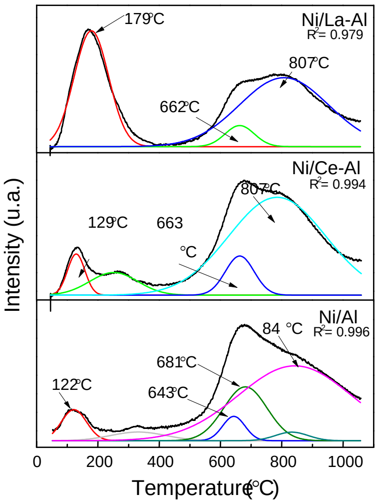


Figure 2.11. H_2-TPD profile of alumina supported Ni catalysts

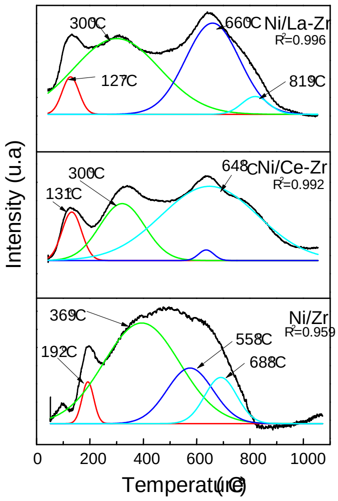


Figure 2.12. H_2-TPD profile of zirconia supported Ni catalysts

In the recorded TPD profile of the zirconia supported Ni catalyst, we observe the presence of both temperature domains. In the lower temperature domain two distinct types are identified type Ia and type Ib, who are associated with catalytic active centres, having different strength interaction with the Ni surface.

CHAPTER III

CATALYST EVALUATION PERFOMANCES IN ETHANOL STEAM REFORMING PROCESS

The evaluation of the activity of the prepared catalysts was made in an installation designed in our laboratory. The tests were performed at ambient pressure. The installation is composed of three parts: the controlled gas and liquid supply, the reactor made of stainless steel (i.d. 9 mm) placed in a temperature controlled oven and the analysis part.

3. Catalyst evaluation in ethanol steam reforming process

Ni based catalysts regardless of their alumina or zirconia support were tested in ethanol steam reforming reaction in different reaction conditions: temperature range (150°C-350°C), different carrier gas flow (Ar) (10-300 ml/min), different liquid flow (0.1- 0.6 ml/min) and different metal content of Cu (1%-3%) on the catalyst surface. During the experiments only one parameter was modified the rest remaining constant, recording thus the influence of this parameter on the ethanol conversion and in hydrogen yield. Also we follow the effect that this parameter has on the reaction products, as well as on the deactivation of the catalyst.

3.1.1. The variation of the catalytic parameters with the carrier flow

In order to study the influence of the carrier flow on catalytic parameters in the experiments we have imposed the following conditions: the tested catalyst is Ni/Al, the imposed temperature is 350°C and the imposed liquid flow is 0.1 ml/min. The flow of the carrier gas is set in the range 10-300 ml/min.

The ethanol conversion reaches the maximum value of 100% in the experiment in which we use the minimum tested flow of Ar, this is probably dued to the higher contact time between the reactant and the catalyst (Figure 3.1). Increasing the Ar flow we observe a decrease in ethanol conversion, the lowest value being ≈ 97% and it is recorded at the highest flow of Ar.

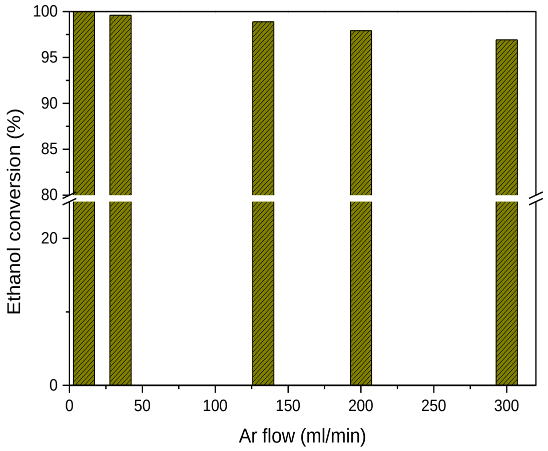


Figure 3.1. Ethanol conversion with the carrier gas (Ar)

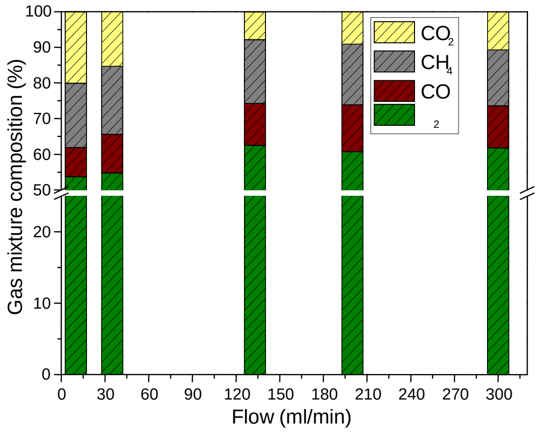


Figure 3.2. Gas product distribution in gas mixture

The gas reaction mixture has as main component hydrogen, but also other components (CO, CH_4, and CO_2), their proportion in the mixture is dependent on the experimental conditions (Figure 3.2). Regarding the hydrogen yield, which represents the catalyst ability to generate hydrogen in the reforming process, we observe an increase of hydrogen yield with the increase of carrier gas flow (Figure 3.3).

Catalyst stability is evaluated by measuring the ethanol conversion after 24h time on stream. In the experiments with Ar flows higher than 133 ml/min we observe a decrease in ethanol conversion with almost 30% (Figure 3.4). Usually in the ESR reaction the catalyst deactivation occurs due to carbon formation and deposition on the catalyst surface. To investigate the nature of the carbon deposition TGA, TEM method were applied. TEM analysis revealed the presences of filamentous carbon and by TGA analysis that the mass loss is 12%.

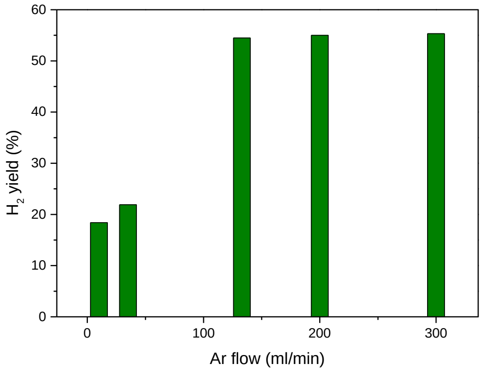


Figure 3.3. H_2 yield with Ar flow

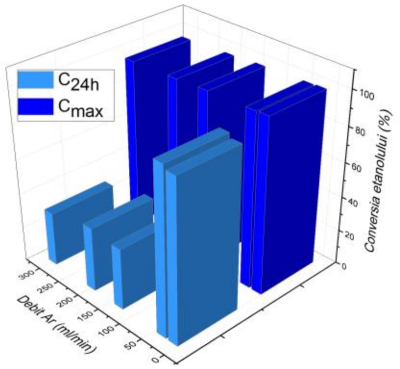


Figure 3.4. Catalyst stability of Ni/Al

C_{max}- maximum ethanol conversion, C_{24h} -ethanol conversion after 24

3.1.2. The variation of the catalytic parameters by promoting the basic catalyst with variable quantities of the metal loading

We have prepared three Ni-Cu catalysts with different copper loadings (1%, 2% and 3%) on alumina support through co-impregnation method. Their catalytic activity was evaluated at temperature between 150-350°C, the gas flow was constant 133 ml/min and the value of the liquid flow is set to 0.6 ml/min.

Ethanol conversion and the hydrogen yield are temperature dependent and are positively influenced by the increase in copper content on the surface of the catalyst (Figure 3.8 and Figure 3.10).

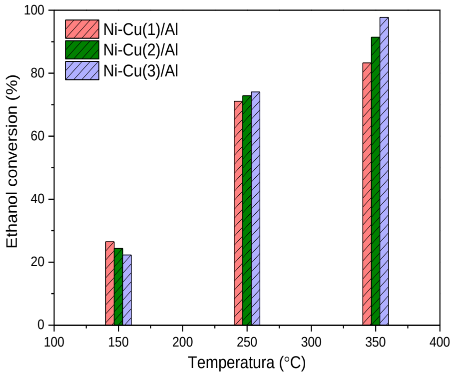


Figure 3.8**.** Temperature dependence of ethanol conversion

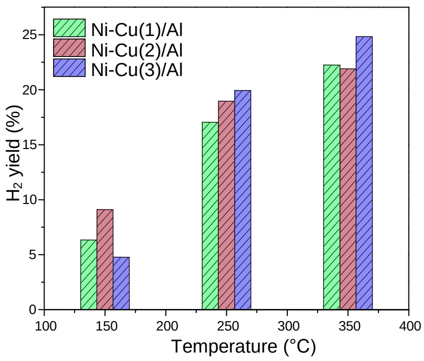


Figure 3.10. Hydrogen yield of Ni-Cu/Al catalysts

In order to determine the type and nature of the carbon deposits on the catalyst surface TEM analysis was used (Figure 3.12). At 150°C an amorphous carbon is identified and at 350°C a filamentous carbon deposit is revealed. This type of deposit is growing away from the catalytic active centers of the catalyst.

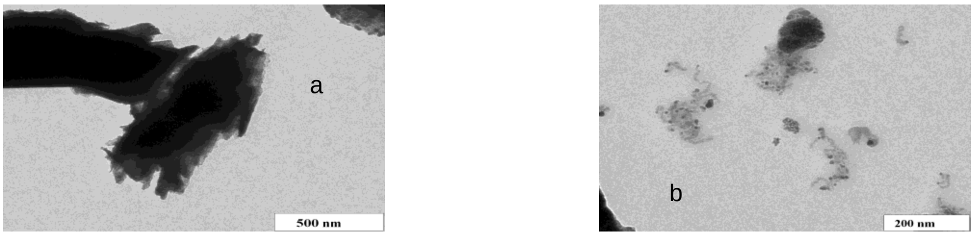


Figure 3.12. TEM images Ni-Cu(1)/Al catalyst: a -150°C; b -350°C

The catalyst Ni-Cu/Al has the best performances regarding the ethanol conversion (at 350°C ethanol is totally converted), the recorded value for hydrogen yield is the highest and the catalyst deactivation is below 20%.

3.1.3. The variation of the catalytic parameters with the addition of an supplementary metal to Ni/Al

A series of experiments were performed in order to observe the influence on the catalytic parameters with addition of a supplementary metal (Ag, Au and Cu) to the base catalyst (Ni/Al). The investigated catalyst were Ni/Al, Ni-Cu/Al, Ni-Ag/Al, Ni-Au/Al, the temperature range is set between 150°C-350°C, the gas flow is set to 133 ml/min and the liquid flow between 0.1-0.6 ml/min.

Regarding the ethanol conversion (Figure 3.14) we observe a decrease of the recorded values at higher liquid flows (0.3, 0.6 ml/min) compared with values recorded at 0.1 ml/min. The addition of the supplementary metal has a positive effect in raising the ethanol conversion at higher liquid flows. The total conversion of ethanol is observed for all the tested catalyst at 0.1 ml/min and 350°C.

The calculated hydrogen yield for all the catalyst at all the experimental conditions reveled that Ni/Al is the catalyst for which the recorded value is the highest at 350°C and at 0.1 ml/min.

We observed that the deactivation of the catalyst is diminished by the addition of the supplementary metal for Ni-Ag/Al and Ni-cu/Al at 250°C. At 350°C and 0.1 ml/min the lowest catalyst deactivation is observed for Ni/Al, Ni-Cu/Al and Ni-Au/Al (Figure 3.18).

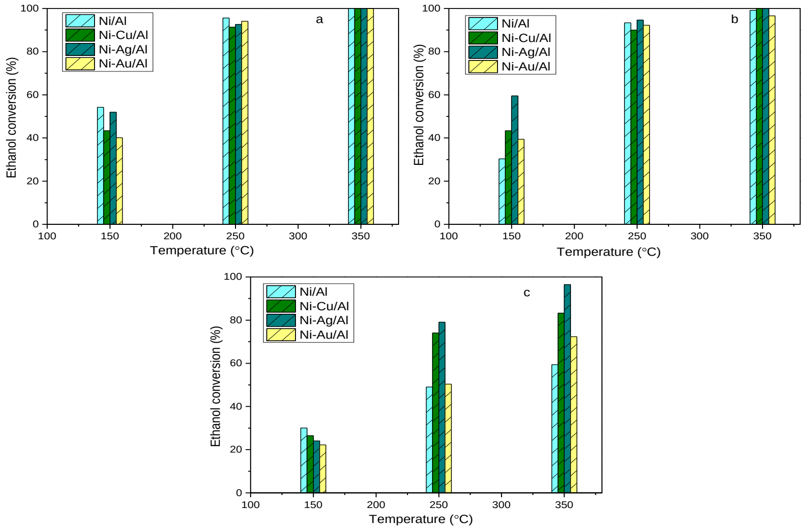


Figure 3.14. Ethanol conversion at different liquid flows: a- 0.1 ml/min; b-0.3 ml/min; c- 0.6ml/min

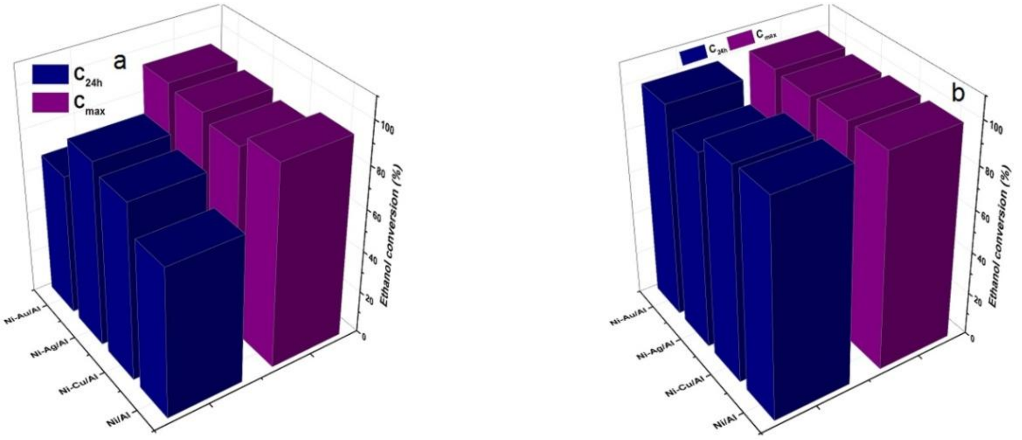


Figure 3.18. The catalyst stability of Ni supported alumina catalyst at 0.1 ml/min a-250°C; b-350°C; C_{max}- maximum ethanol conversion, C_{24h}-ethanol conversion after 24h

3.1.4. The variation of the catalytic parameters with the modification of the support

The catalytic activity of the metal/support catalysts depends on catalytic active metal as well as on the used support. We have modified the alumina and zirconia support with the addition of La_2O_3 in order to reduce the acidity of the support. The addition of CeO_2 to the alumina could improve the support capacity to dissociate water or to the support influence in increasing the reduction degree of Ni nanoparticles.

The investigated catalysts are: on alumina support (Ni/Al, Ni/Ce-Al, Ni/La-Al) and zirconia support (Ni/Zr, Ni/Ce-Zr, Ni/La-Zr), the tested temperature range 150°C-350°C, using a 50°C temperature gradient. The gas flow is constant 35 ml/min and the liquid flow is set to 0.1 ml/min.

From the experimental data (Figure 3.21) we observe that at 150°C the ethanol conversion is very low ≈40% and at 350°C all the catalyst are very active thus ethanol is totally converted on all the catalyst, except Ni/Zr. The addition of the oxides regardless of the support improves the ethanol conversion. At 250°C the ethanol conversion is 100% for the promoted catalyst. Regarding the hydrogen yield the highest value is obtained for Ni/La-Zr (Figure 3.24).

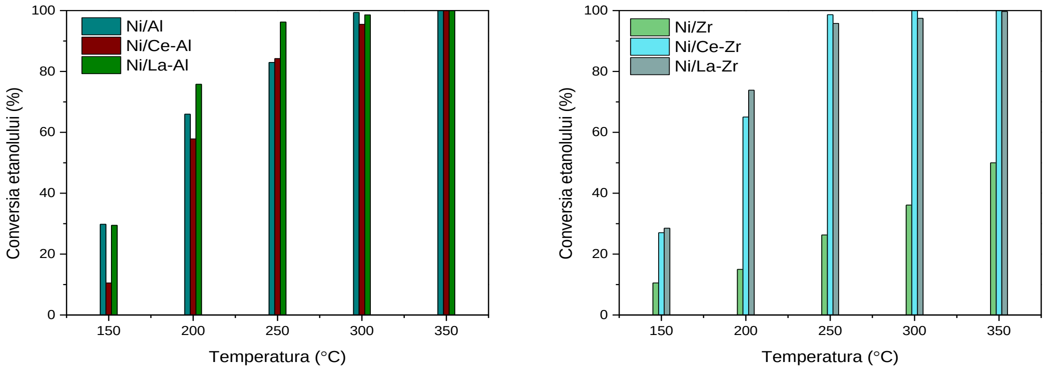


Figure 3.21. Ethanol conversion temperature dependence: a- Ni supported alumina catalysts; b- Ni supported zirconia catalysts

The catalysts stability has been evaluated by measuring the ethanol conversion on stream after 24h. At 350°C we observe a high stability for most of tested catalyst for all the duration of the testing period. Ni/Zr and Ni/Ce-Zr are an exception, their deactivation being with ≈30% and 10% respectively lower than the maximum value of the recorded ethanol conversion.

The carbon deposit analyzed by TEM method is identified as a filamentous one, who does not engulf the Ni nanoparticles. For Ni/Zr we identify an amorphous carbon deposit which most probably is one of the main causes of catalyst deactivation.

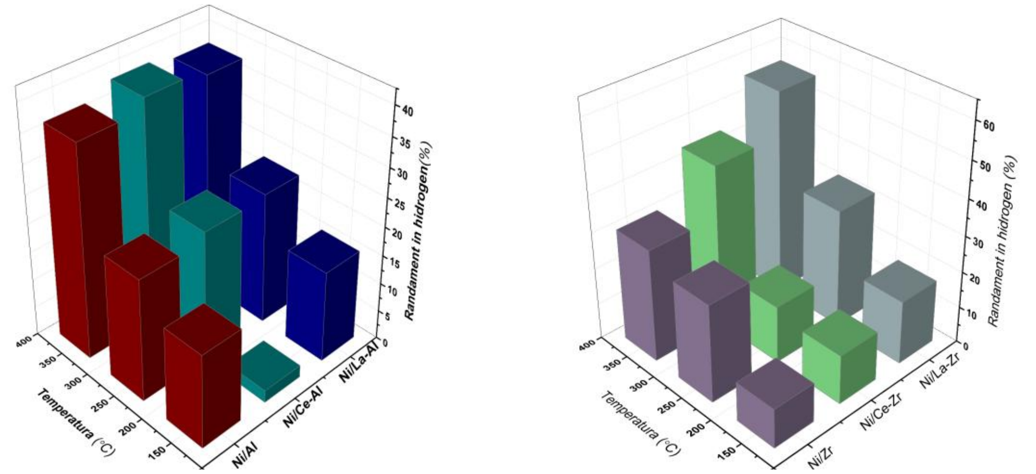
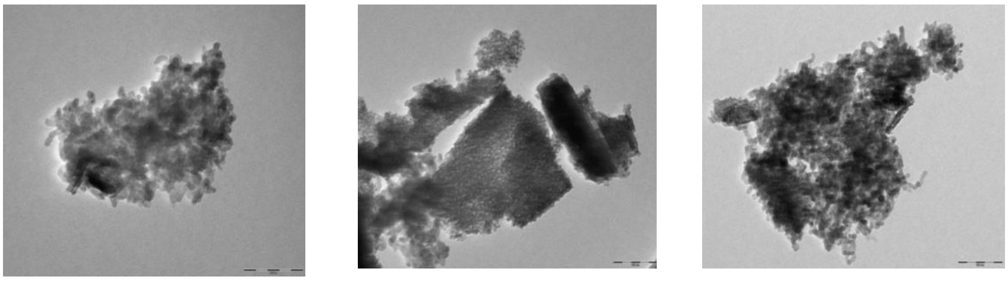
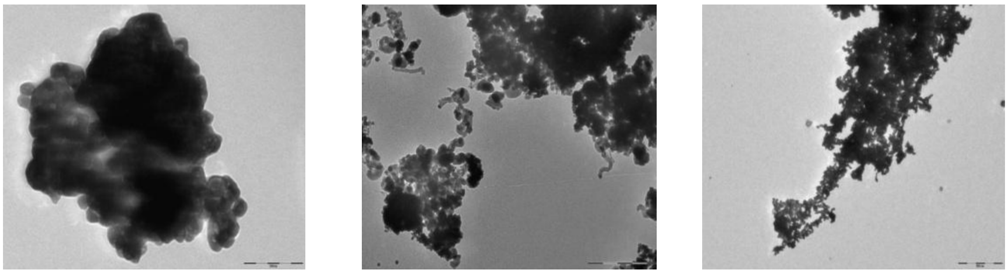


Figura 3.24. Randamentul în hidrogen obţinut pentru : a- catalizatorii pe bază de Ni depus pe suport de aluminiu, b- catalizatorii pe bază de Ni depus pe suport de zirconiu



(a) Ni/Al (b) Ni/Ce-Al (c) Ni/La-Al



(d) Ni/Zr (e) Ni/Ce-Zr (f) Ni/La-Zr

Figura 3.28. Imagini TEM înregistrate pe catalizatori uzaţi: unitatea de măsură este 100nm pentru (a)-(d) şi 500nm pentru (e),(f)

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CHAPTER IV

CATALYST EVALUATION PERFOMANCES IN BIO- ETHANOL STEAM REFORMING PROCESS

The evaluation of the activity of the prepared catalysts was made in a conventional installation. The tests were performed at ambient pressure. The installation is composed of three parts: the gas and liquid input (the gas is controlled by mass flow controller, and the liquid mixture is fed using a LC 6A pump), the reactor section made of stainless steel (i.d. 9 mm) placed in a temperature controlled oven and finally the analysis part. The catalyst (1g) is diluted with the same quantity and similar granulation of alumina and placed inside the reactor.

The raw material used to obtain bio-ethanol is wood wastes of Albiens Alba. The scheme of the bioethanol production is presented in Figure 4.1.

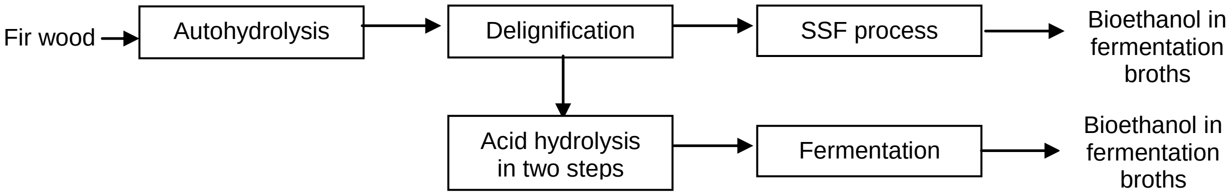

Figura 4.1. Schematic representation of different treatments performed for bioethanol production from wood wastes

Regardless of the fermentation methods used to prepare bio-ethanol, the obtained product it's a liquid-solid mixture which contains nutrients, inoculum solutions and remains of raw material. The collected liquid fraction, denominated as crude bio-ethanol, was analysed and catalytically reformed with no further modifications. The components identified in the liquid broth are: alcohols, acids, ethers, aldehydes (Tabelul 4.1)

Table 4.1. The composition of fermentation medium obtained by SSF and acid hydrolysis

Nr. crt.	**Compound**	**SSF method**	**Acid hydrolysis method**
1	dimethyl ether	0,008 g/L	0,007 g/L
2	methanol	0,298 g/L	0,279 g/L
3	***ethanol***	***43.690 g/L***	***37.53 g/L***
4	n-propanol	0,404 g/L	0,367 g/L
5	2-methyl-1-propanol	0,164 g/L	0,149 g/L
6	n-butanol	0,159 g/L	0,187 g/L
7	3-methyl-1-butanol	0,195 g/L	0,177 g/L
8	2-methyl-1-butanol	0,126 g/L	0,096 g/L
9	pentanol	0,193 g/L	0,176 g/L
10	***acetic acid***	***10,240 g/L***	***16,360 g/L***
11	2-methyl-1-propanol	0,034 g/L	0,021 g/L
12	2,5-dimethylfuran	0,021 g/L	0,018 g/L
13	3-methylbutyl acetate	0,011 g/L	0,010 g/L
14	cyclohexanol	0,124 g/L	0,116 g/L
15	propanal	15,65 mg/L	12,64 mg/L
16	methyl propanoate	0,742 mg/L	0,521 mg/L
17	ethyl hexanoate	321,56 mg/L	240,817 mg/L
18	ethyl octanoate	1,752 mg/L	1,151 mg/L
19	propanal	15,632 mg/L	13,185 mg/L
20	propanoic acid	625,32 mg/L	423,62 mg/L
21	2-methyl-propanal	86,32 mg/L	73,79 mg/L
22	isobutyric acid	10,65 mg/L	8,32 mg/L
23	butanoic acid	4,52 mg/L	2,16 mg/L
24	2-methyl-1-butanal	526,3 mg/L	493,9 mg/L
25	pentanal	118,65 mg/L	111,22 mg/L
26	pentanoic acid	4,56 mg/L	2,88 mg/L
27	octanoic acid	0,89 mg/L	0.89 mg/L
28	decanoic acid	3,562 mg/L	2.949 mg/L

4.3. Catalysts evaluation in bio-ethanol steam reforming process

Ni based catalyst were tested in bio-ethanol steam reforming process in different reaction conditions: temperature range (150°C-350°C), inert gas flow (Ar) modification (10-200 ml/min), and a change in liquid flow from 0.1 to 1 ml/min.

The experiments were performed by modifying a single parameter the rest remaining constant, recording thus the influence of this parameter on the ethanol conversion, acetic acid conversion and on the hydrogen production. Also, we follow the effect of the modification the parameter one the gas reaction products as well as on deactivation of the tested catalyst.

4.3.1. *The variation of the catalytic parameters with the carrier flow*

We have prepared through impregnation a Ni/Al catalyst in order to be tested in different experimental conditions: temperature 350°C, the imposed liquid feed rate 0.1 ml/min. The inert gas flow is set to vary between 10-200 ml/min.

The total conversion of ethanol was obtained in the experiments with inert gas flow above 70 ml/min and the total conversion of acetic acid is obtained at every tested flow of inert gas (Figure 4.2).

The hydrogen production depends on the initial composition of the bio-ethanol; the maximum is obtained in the experiment in which the flow of Ar is set at 133 ml/min (Figure 4.4).

Concerning the catalyst stability during the testing period (6h), we observe that for the experiments with Ar flow higher than 133 ml/min the deactivation is very low (Figure 4.5).

From the recorded TEM images (Figure 4.8) of the spent catalyst we observe filamentous carbon deposits. Due to the fact that the catalyst is very stable, at XRD analysis the carbon under crystalline form cannot be identified and the fact that TEM revealed only filamentous carbon we can say that the major cause of catalyst deactivation is the oxidation of the catalytic active centers.

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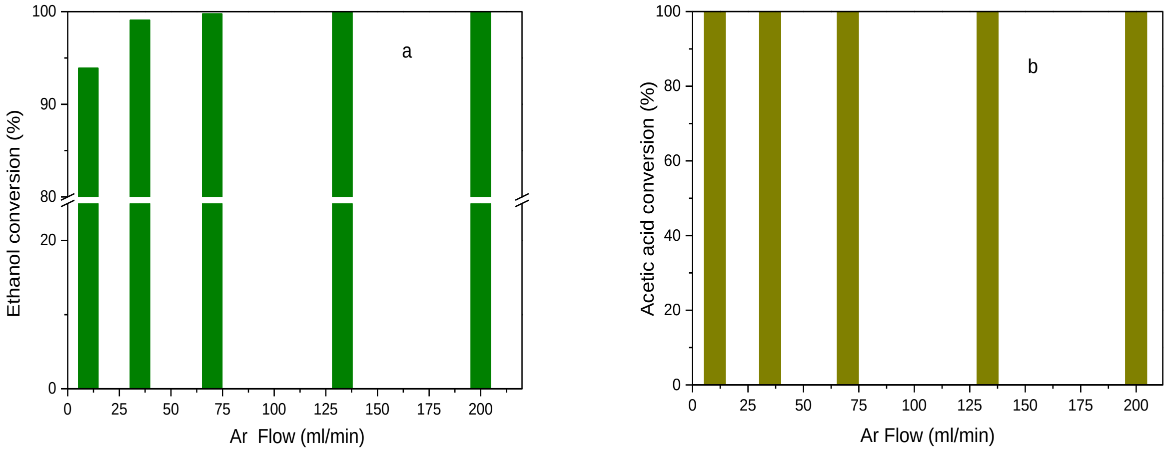


Figure 4.2. Ethanol conversion (a) acetic acid (b) dependence with Ar flow in bio-ethanol steam reforming

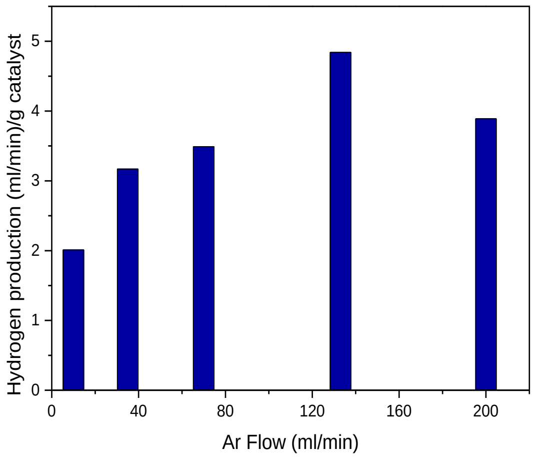


Figure 4.4. Hydrogen production with Ar flow

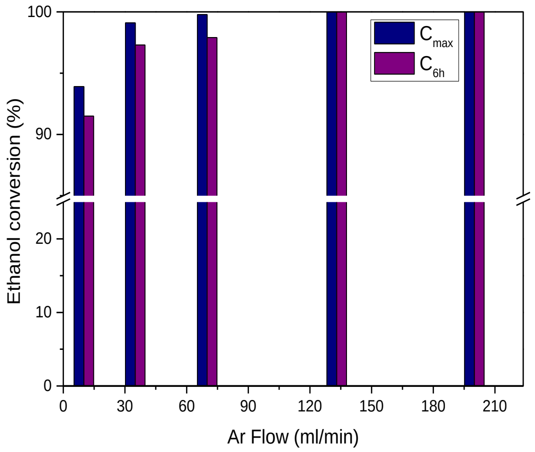
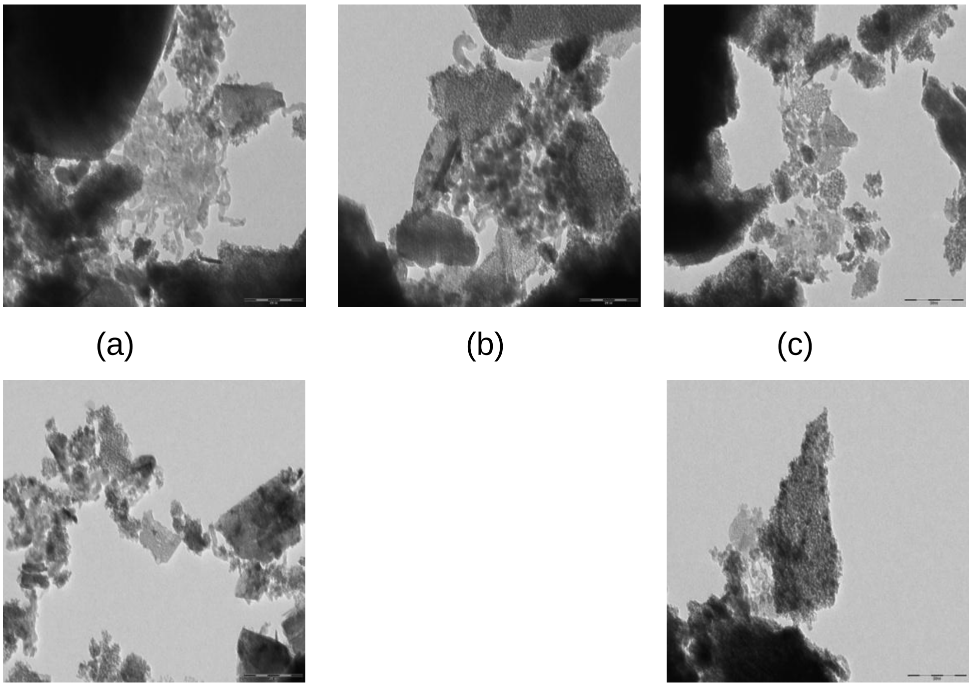


Figure 4.5. Catalyst stability of Ni/Al with Ar flow:

C_{max}- maximum ethanol conversion,

C_{6h}- ethanol conversion after 6h



(a) (b) (c)

(d) (e)

Figure 4.8. TEM images of spent catalysts in different experimental conditions: a-10ml/min Ar; b-35 ml/min; c-70 ml/min; d-133 ml/min; e-200 ml/min, measuring scale 200nm

4.3.2. The variation of the catalytic parameters with liquid feed rate and modification of the support

A series of experiments were performed in order to investigate the influence on the catalytic parameters of the liquid feed rate, in the process of bio-ethanol steam reforming. The conditions studied were: investigated catalyst Ni/Al, temperature 350°C, inert gas flow 133 ml/min. The liquid feed rate is set to vary between 0.1-1 ml/min. In this set of experiments we have only tracked the ethanol concentration from the bio-ethanol.

As a conclusion we have determined the optimal experimental conditions using as catalyst Ni/Al at which the ethanol conversion is maximum and the deactivation is minimum: temperature 350 °C and the liquid feed rate is 0.8 ml/min.

In order to highlight the influence of the support modification on the catalytic parameters we have performed different experiments at the following experimental conditions: inert gas flow 133 ml/min, liquid feed rate 0.8 ml/min and the temperature is set between 150-350°C. The catalyst support alumina is modified by the addition of La_2O_3 and CeO_2 to Ni/Al obtaining thus two new catalysts Ni/La-Al and Ni/Ce-Al. For all the duration of the experiments we tracked the ethanol and acetic acid conversion.

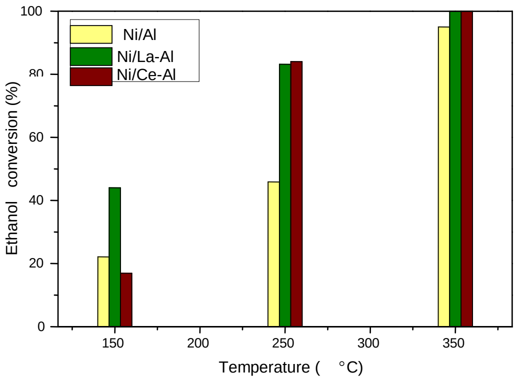


Figure 4.10. Temperature dependence of ethanol conversion

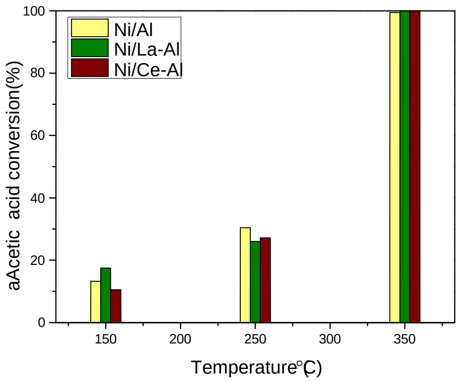


Figure 4.11. Temperature dependence of acetic acid conversion

The hydrogen production expressed as hydrogen volume/minute/g catalyst is obtained from reforming all the compound of bio-ethanol: ethanol, acetic acid and oxygenated compounds (Tabelul 4.1). At 150°C and 250°C the hydrogen production is very low (Figure 4.14) and at 350°C is much higher due to the contribution of both ethanol and acetic acid total conversion. Between the two promoted catalysts with oxides the one with La_2O_3 seems to give better results for the production of hydrogen

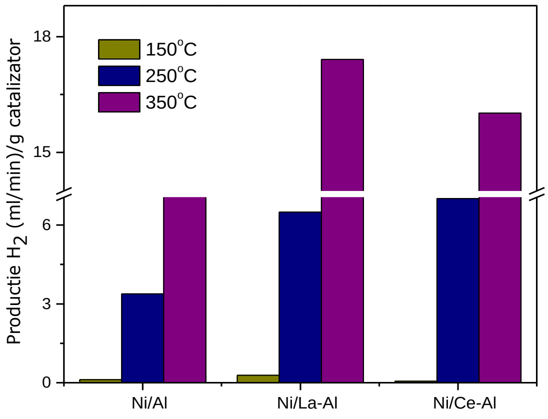


Figure 4.14. Hydrogen production of tested catalyst

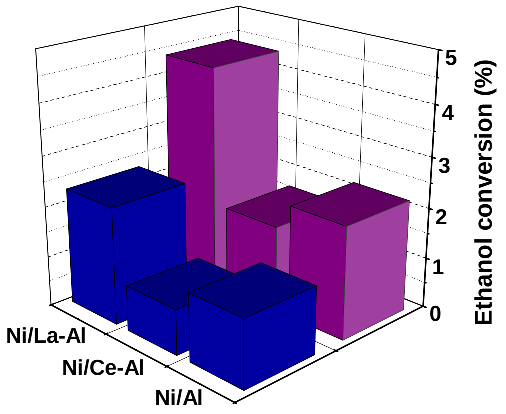


Figure 4.14. Catalyst stability for all tested catalyst; purple –maximum ethanol conversion; blue- ethanol conversion after 4h

Catalyst deactivation is quantified by measuring on line the ethanol conversion during the testing period. At 350 °C the tested catalyst are stable for all the testing period and at 150°C we observe an increase in deactivation for all the tested catalysts (Figure 4.16). Most probably one of the main causes for catalyst deactivation consists in the formation and deposition of carbon on the catalytic active center. This carbon deposits were investigated through TPO and XRD analysis. The TPO analysis revealed that the carbon deposits are temperature dependent, the quantity and structure identified are very different (Figure 4.17).

The XRD recorded profiles of the spent catalyst are presented in (Figure 4.18), the presence of NiO is highlited at 43°.The graphitic carbon cannot be identified at 26.5° regardless of the tested catalyst, probably due to low form of cristalinity.

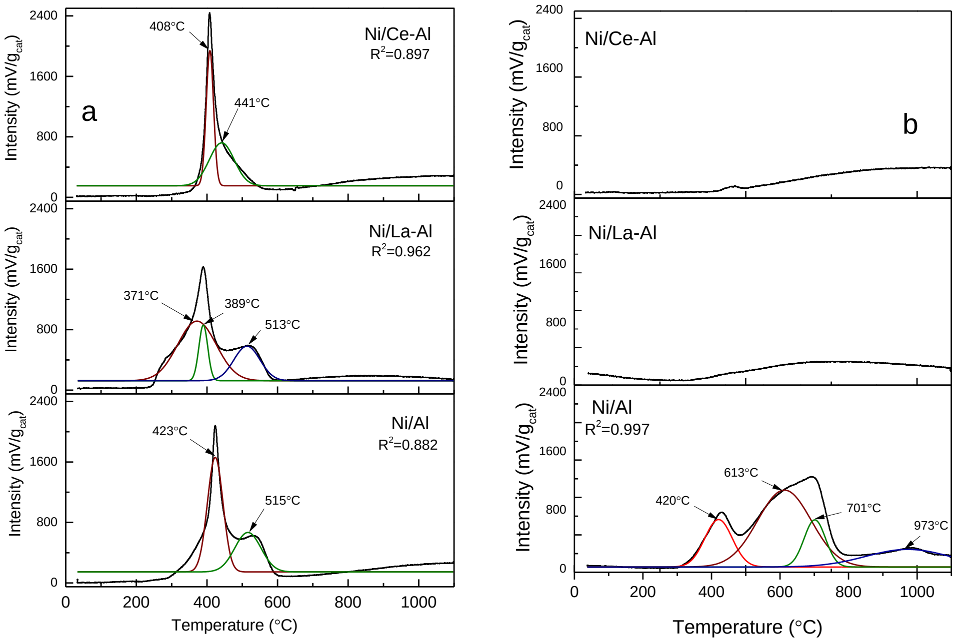


Figure 4.17. TPO profile of Ni supported alumina catalyst where: a-150°C, b-350°C

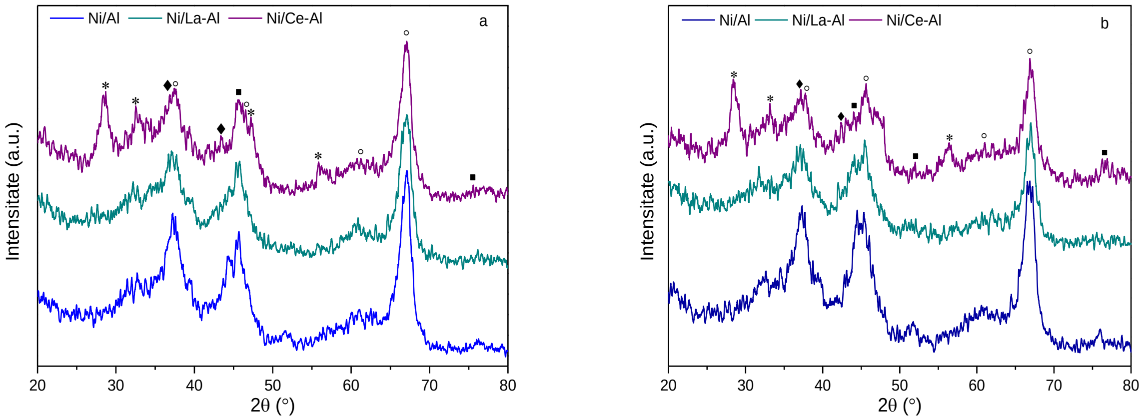


Figure 4.18. XRD spectra of spent catalyst: a - 150°C şi b- 350°C, ■- Ni, ♦- NiO, ○-Al_2O_3 *- CeO_2

4.3.3. The variation of the catalytic parameters with the addition of supplementary metal to base catalyst

A series of experiments were performed in order to observe what influence has the addition of a supplementary metal to Ni/Al on the catalytic parameters in bio-ethanol steam reaction. The studied experimental conditions were: tested catalyst Ni/Al, Ni-Cu/Al, Ni-Ag/Al, Ni-Au/Al; temperature range 150°-350°C. The gas inert flow is 133 ml/min and the liquid flow is set between 0.1-0.6 ml/min.

In (Figura 4.19) we observe the dependence of ethanol conversion with temperature and catalyst. We notice that at low temperatures (150°C) the ethanol conversion is very low < 50%.The ethanol conversion is improved by the addition of the supplementary metal at 250°C at liquid feed rate of 0.1 and 0.3 ml/min. For higher liquid feed rate 0.6ml/min we cannot says the same thing, we do not observe an improvement of ethanol conversion for the promoted catalyst. At 350°C the ethanol conversion attains maximum for all tested catalyst except Ni-Ag/Al for which the ethanol conversion is 98%.

As for the hydrogen production (Figure 4.23) we observe that temperature has an important role, at low temperature the hydrogen production is very low, raising the temperature leads to an increase of the values recorded for this parameter, the highest value is recorded at 350°C. We observe that a higher liquid feed rate leads to a higher production of hydrogen the highest value being recorded for Ni/Al at 0.6 ml/min.

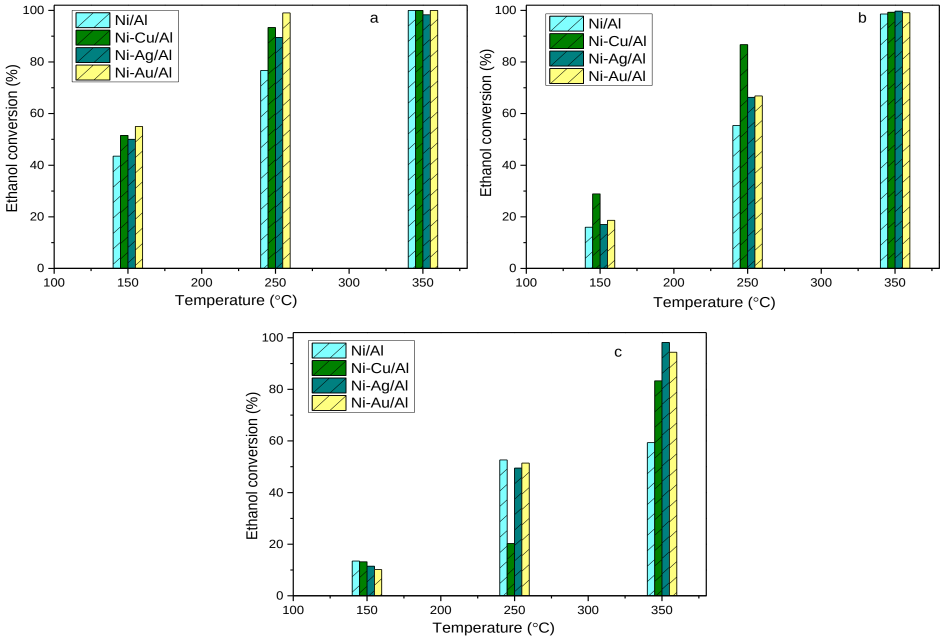


Figure 4.19. Ethanol conversion for tested catalysts versus temperature at different liquid feed rate: a-0.1 ml/min, b-0.3 ml/min, c-0.6 ml/min

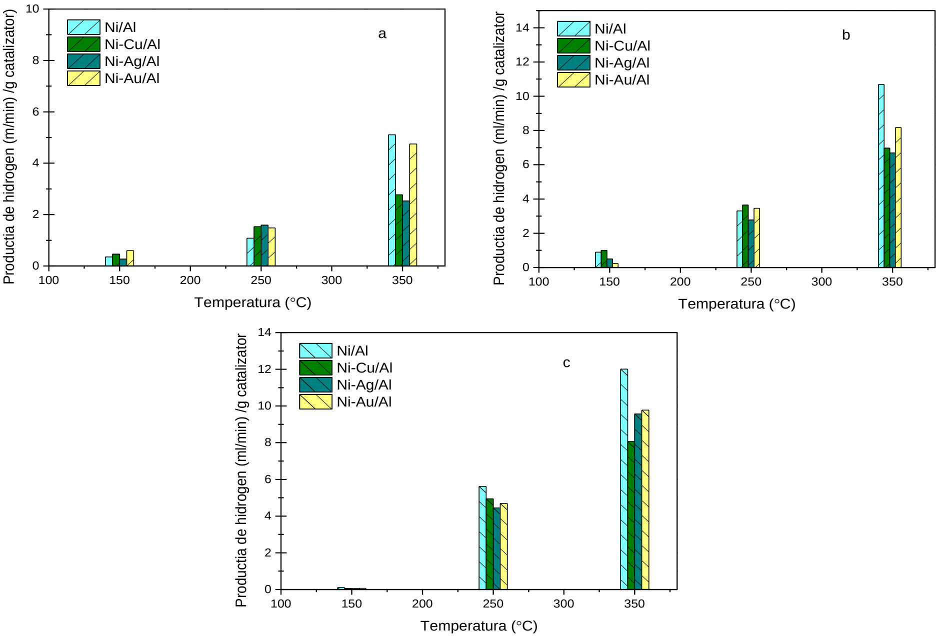


Figure 4.23. Hydrogen production for tested catalysts versus temperature at different liquid feed rate: a-0.1 ml/min, b-0.3 ml/min, c-0.6 ml/min

During the testing period we observe a decrease in ethanol conversion at 150°C, for all tested catalysts, the conversion being with 50% lower than the maximum ethanol conversion recorded for liquid feed rate of 0.1 and 0.3 ml/min.

At 0.6 ml/min and 150°C (Figure 4.26) the deactivation is even more accentuated, for Ni/Al we observe almost a total deactivation. We notice for the bimetallic catalyst a better stability at this experimental temperature.

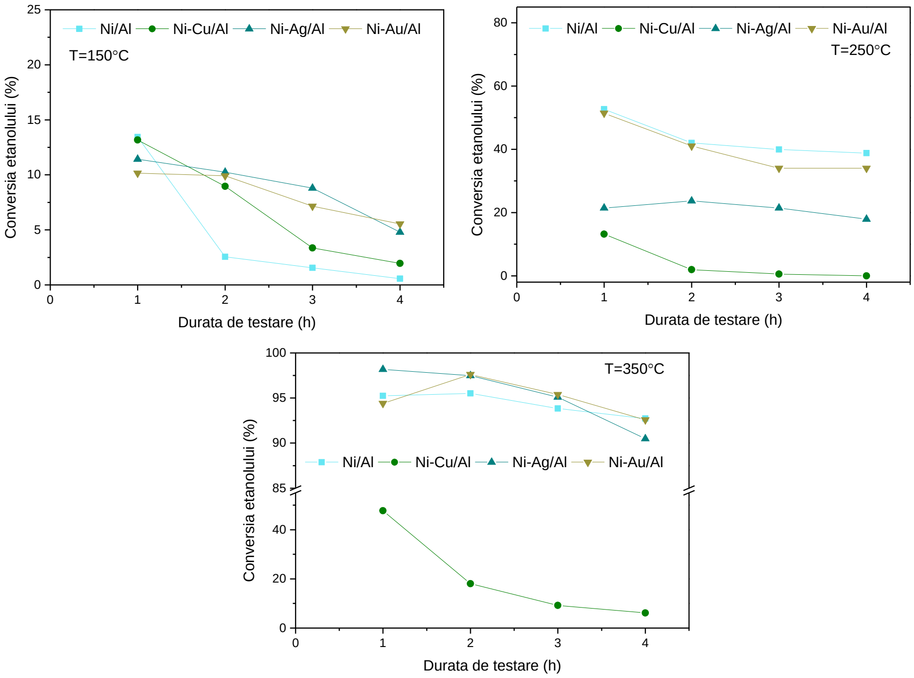


Figure 4.26. Catalysts stability in bio-ethanol steam reforming process at 0.6 ml/min

The catalyst deactivation at 350°C is very low for all the tested catalyst regardless of the liquid feed rate tested. Ni-Ag/Al at 0.1 ml/min and Ni-Cu/Al at 0.6 ml/min are an exception their deactivation being much higher.

From the XRD analysis we cannot identify for neither of the tested catalyst in any tested experimental condition the carbon in crystalline form at 26.5°. In the XRD spectra we identify the corresponding lines of alumina and Ni at all the tested temperatures and liquid feed rate. At 250°C and liquid feed rate 0.3 ml/min we notice the presence in the XRD spectra of a line usually associated with NiO at 43° (Figure 4.28).The catalyst which present this line in the spectra are Ni/Al, Ni-Ag/Al, Ni-Au/Al. The presence of NiO is confirmed also by the deactivation recorded for these catalysts.

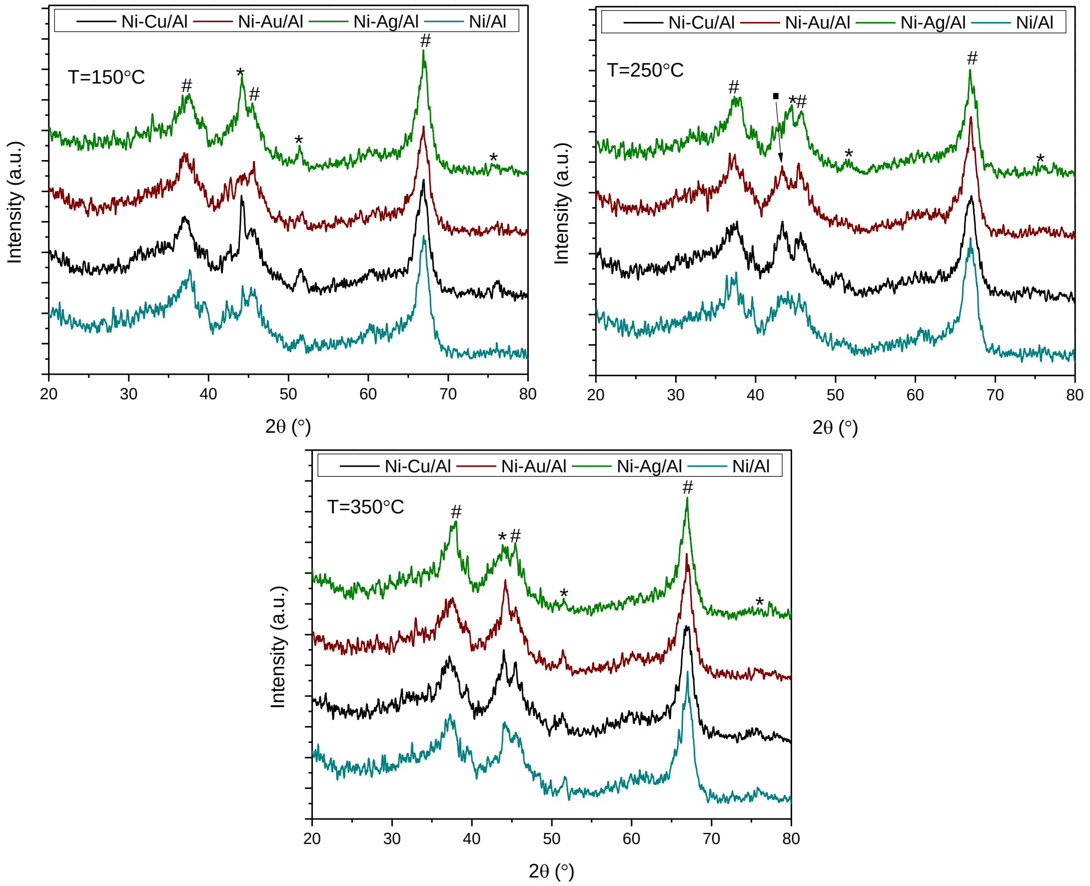


Figure 4.28. XRD recorded spectra for spent catalysts in bio-ethanol reforming process at 0.3 ml/min:, *- Ni, ■- NiO, # -Al_2O_3

From the experimental data regarding the ethanol conversion and XRD analysis we can conclude that the recorded deactivation for all the tested catalysts is temperature dependent. Nevertheless we can say that the addition of the supplementary metal to Ni/Al seems to improve the catalyst stability but only in certain experimental conditions.

CONCLUSIONS

The main objectives of this research were (1) to design and develop a high performance catalyst that is capable of efficiently catalyzing the production of hydrogen in the steam reforming process, (2) evaluation of the newly prepared catalysts in ethanol steam reforming process, (3) evaluation of the newly prepared catalysts in bio-ethanol steam reforming process.

The main observations and conclusions stemming from this thesis are:

- We have prepared 11 different catalysts nickel based, using four different methods of preparation. The catalysts prepared on alumina support are: Ni/Al, Ni-Ag/Al, Ni-Au/Al, Ni-Cu/Al (with a different copper content 1%-3%), Ni/La-Al, Ni/Ce-Al, Ni/Al, and the ones prepared on zirconia support are: Ni/Zr, Ni/La-Zr, Ni/Ce-Zr.
- For Ni-based catalysts deposited on aluminium oxide the addition of noble metals (Ag, Au, Cu) or cerium and lanthanum oxide does not have the effect of modifying the total surface area, volume and pore size.
- The addition of cerium and lanthanum oxide to the alumina or zirconia support, leads to important changes in catalyst structure.
- From the catalytic evaluation in the ethanol steam reforming process of the prepared catalysts the following results were observed: the maximum conversion is obtained at 10 ml/min flow of Ar, the maximum hydrogen yield at 300 ml/min inert gas and from the stability test for a period of 24h Ni/Al is more stable when the value of inert gas flow is set to 35 ml/min. The identified carbon deposit for the catalyst surface is a filamentous deposit.
- For Ni-Cu/Al type catalyst with different copper content, the ethanol conversion as well as the hydrogen yield are positively influenced by the increase in copper content, the Ni-Cu(3)/Al catalyst presenting the best performances: maximum ethanol conversion, the highest recorded value for hydrogen yield and the lowest catalyst deactivation.
- The addition of the supplementary metal to the basic catalyst Ni/Al has a positive influence in the ethanol steam reforming by increasing the obtained

value for ethanol conversion and also by diminishing the catalyst deactivation but only in certain experimental conditions.

- The addition of La_2O_3 and CeO_2 leads to a slight improvement of ethanol conversion for the catalyst on alumina support and to a major improvement for the catalyst on zirconia support.
- The Ni/La-Al catalyst presents the best catalytic performances for the imposed experimental conditions.
- From the evaluation tests in the steam reforming process of bio-ethanol we have obtained the following results: maximum ethanol conversion at Ar flow >70 ml/min, acetic acid conversion is maximum regardless of the tested Ar flow at 350°C, the maximum hydrogen production is recorded at Ar flow =133 ml/min. The stability along the testing period (6h) is high for flows of inert gas ≥133ml/min.
- The ethanol conversion at lower temperature is improved by the addition of the oxides (La_2O_3 and CeO_2) at the Ni/Al catalysts in bio-ethanol steam reforming process. The conversion of the acetic acid conversion does not seem to be improved by the addition of the two oxides.
- The stability of the catalyst is very good for the whole tested period (4h) for the catalyst with additional oxide, these catalyst do not suffer any deactivation.
- For catalyst with additional metal (Ni-Cu/Al, Ni-Au/Al and Ni-Ag/Al) we observe at lower temperatures the values for ethanol conversion are higher than the one recorded for Ni/Al. At higher temperatures the values recorded for ethanol conversion are similar.
- The addition of the supplementary metal to Ni/Al induces an improvement in catalyst stability in the bio-ethanol steam reforming process, but only in same experimental conditions.

DISSEMINATION IN THE FIELD OF THE THESIS

Published ISI Articles and Conference Papers

1. **M. Dan**, L. Senila, M. Roman, M. Mihet, M. D. Lazar, *From wood wastes to hydrogen – Preparation and catalytic steam reforming of crude bio-ethanol obtained from fir wood*, ***Renewable Energy***, 74, 27-36, **2015**.

2. **M. Dan**, M. Mihet, Z. Tasnadi-Asztalos, A. Imre-Lucaci, G. Katana, M. D. Lazar, *Hydrogen production by ethanol steam reforming on nickel catalysts: Effect of support modification by* CeO_2 *and* La_2O_3, ***Fuel***, 147, 260-268, **2015**.

3. **M. Dan**, M. Mihet, M. D. Lazar, L. M. Muresan, *Promoted alumina Ni catalyst for ethanol steam reforming*, accepted for publication

4. **M. Dan**, M. Mihet, V. Almasan, G. Borodi, G. Katona, L. M., M. D. Lazar , *Modified Ni-Cu catalysts for ethanol steam reforming*, **AIP Conf. Proc**., 1565, 208, **2013**
5. M. D. Lazar, **M. Dan**, M. Mihet, G. Borodi and V. Almasan, *Hydrogen production by ethanol steam reforming on Ni/oxide catalysts*, **AIP Conf. Proc.** ,1425, 131, **2012**.

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Presentation at International Conferences

1. **M. Dan**, M. Mihet, V. Almasan, M. D. Lazar, *Ethanol Steam Reforming on Metal Promoted Nickel Catalysts: Study of Catalysts Deactivation*, 11th European Congress on Catalysis – EuropaCat-XI, 1-6 Septembrie **2013**, Lyon, France

2. **M. Dan**, M. Mihet, V. Almasan, M.D. Lazar*, Hydrogen production by ethanol steam reforming on promoted nickel catalysts*, The 10th International

Symposium of the Romanian Catalysis Society „ROMCAT 2013” 29-31 May **2013**, Cluj Napoca, Romania

3. M. D. Lazar, **M. Dan**, M. Mihet, V. Almasan, *Au and Ag modified alumina supported Ni catalysts for* H_2 *production by ethanol steam reforming*, International Congress on catalysis „ICC-2012”, Munchen, Germany, 1–6 July **2012**

4. V. Almasan, **M. Dan**, M. Mihet, M. D. Lazar, *Hydrogen Production by Ethanol Steam Reforming on Modified Zirconia Supported Nickel Catalysts*, International Congress on catalysis „ICC-2012”, Munchen, Germania, 1–6 July **2012**

5. **M. Dan**, M. D. Lazar, V. Almasan, *Modified nickel catalysts for ethanol steam reforming***,** Europen Congress on Catalysis EUROPACAT – 10, Glasgow, Marea Britanie, 28 August – 2 Septembre **2011**

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