



## METHANE STEAM REFORMING OVER Ni/Al<sub>2</sub>O<sub>3</sub> PROMOTED BY CeO<sub>2</sub> AND La<sub>2</sub>O<sub>3</sub>

Monica DAN,\* Mihaela D. LAZAR, Vasile REDNIC and Valer ALMASAN

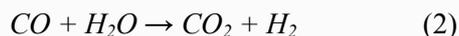
National Institute for Research and Development of Isotopic and Molecular Technologies, 65-103 Donath Street,  
400293 Cluj-Napoca, Roumania

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Two Ni/Al<sub>2</sub>O<sub>3</sub> (7% wt. Ni) catalysts modified by addition of CeO<sub>2</sub> (6% wt.) and La<sub>2</sub>O<sub>3</sub> (6% wt.) to the alumina support were prepared by wet impregnation and characterized by N<sub>2</sub> adsorption desorption, XRD and XPS techniques. Structural parameters (total surface area, porosity) are not influenced by the addition of secondary oxide to the catalyst support. XRD results reveal the presence of crystalline CeO<sub>2</sub> on the catalysts surface. Lanthanum oxide is amorphous and very dispersed and couldn't be identified by XRD. XPS results indicate the presence of La<sup>3+</sup> on the catalyst surface. Methane conversion is improved by the addition of ceria and lanthana to the nickel catalysts. The promoted catalysts are more stable at low temperatures than un-promoted nickel catalyst.

### INTRODUCTION

In the near future due to the diminishing of fossil fuels resources, new alternative energy sources are required. Hydrogen is preferred as an alternative energy vector, because is environmental clean, doesn't contribute to the greenhouse effect and can be used in different industrial areas: as fuel, for electricity production, etc. The main source for hydrogen production is now considered to be hydrocarbons. The catalytic methane steam reforming process (MSR) is industrially used to obtain H<sub>2</sub> in large scale.<sup>1</sup> The reaction can be represented by Eq. (1) and occurs in parallel with the water – gas – shift reaction (WGS) (Eq. (2)):



Although the supported Ni catalysts are not the most active for MSR, it appears to be the most economical attractive ones due to their lower price. The main problem of this type of reforming catalysts is the strong deactivation process which appears as a consequence of coke formation.

Beside the appropriate catalysts, the industrially used methane steam reforming requires high temperatures (~ 900°C) and pressures (20–30 atm), all this contributing to the high price of produced hydrogen. A solution to make the process more efficient is to find a catalyst with good properties for methane conversion at lower temperatures and pressures. This can be done by promoting the catalyst support with a supplementary rare earth oxide. This kind of addition was proved also, to enhance the catalyst stability toward deactivation,<sup>2</sup> leading to a catalyst with higher activity and stability. In this paper we present the results obtained in preparation, characterization and testing of Ni/Al<sub>2</sub>O<sub>3</sub> catalysts promoted by the addition of CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> to the alumina support.

### RESULTS AND DISCUSSION

Three supported nickel catalysts were prepared by wet impregnation technique: Ni/Al<sub>2</sub>O<sub>3</sub>, Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub>, Ni/La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub>. The Ni content is 7 wt. % and supplementary oxide concentration is 6 wt. %.

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

### Catalysts characterization

For total surface area and porosity determinations, the N<sub>2</sub> adsorption–desorption isotherms were measured. For all three studied catalysts these are of type IV which corresponds to mesoporous solids. The total surface areas, pore volumes and pores medium size does not differ very much by the addition of the secondary oxide, but in all cases are smaller than the values recorded for alumina support. The pore size distribution is narrow and uniform with a medium diameter of 50 Å.

The XRD patterns of all three catalyst samples contain three major peaks attributed to Ni: Ni(1 1 1) at 44.5°; Ni(2 0 0) at 51.8° and Ni(2 2 0) at 76.5° (Fig. 1). There is no evidence of NiO (37.3° and 43.3°)<sup>3</sup> in the XRD patterns of the studied samples indicating that all the nickel oxide was reduced during catalyst preparation and the nickel is present on the support only in the metallic form. For Ni/CeO<sub>2</sub> – Al<sub>2</sub>O<sub>3</sub> the XRD spectra contain peaks attributed to Ni and CeO<sub>2</sub>. Four peaks could be identified and attributed to cerium oxide: CeO<sub>2</sub>(1 1 1) at 28.6°, CeO<sub>2</sub>(2 0 0) at 33°, CeO<sub>2</sub>(2 2 0) at 47.3° and CeO<sub>2</sub>(3 1 1) at 56.7° (Fig. 1).<sup>4</sup>

Table 1

Total surface area, pores volume, pores radius and medium crystallite size for promoted nickel catalysts

Parameter	Support	Catalyst		
	Al <sub>2</sub> O <sub>3</sub>	Ni/Al <sub>2</sub> O <sub>3</sub>	Ni/CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	Ni/La <sub>2</sub> O <sub>3</sub> -Al <sub>2</sub> O <sub>3</sub>
S <sub>t</sub> (m <sup>2</sup> /g)	134	108	105	109
V <sub>p</sub> (cm <sup>3</sup> /g)	0.21	0.18	0.14	0.15
R <sub>m</sub> (Å)	26	25	25	24
D <sub>m</sub> (Å)	-	85,6	78.9	92.1

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

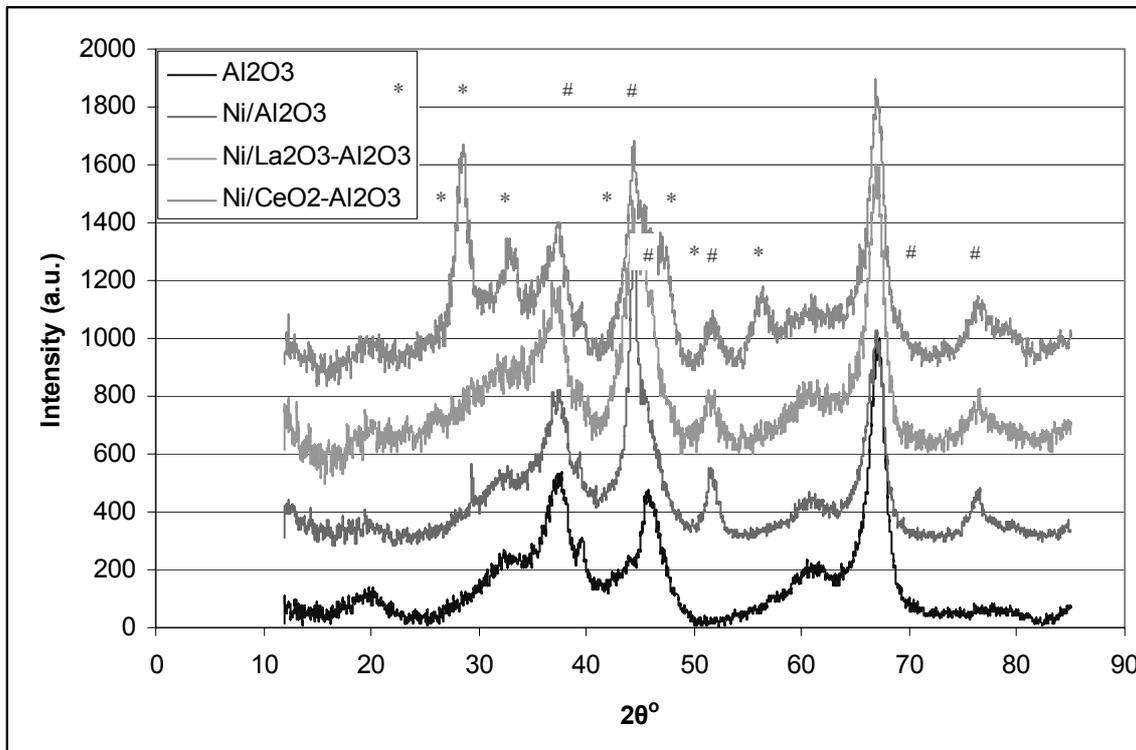


Fig. 1 – XRD patterns of the modified alumina supported nickel catalysts; (#) - peaks correspond to Ni; (\*) - peaks correspond to CeO<sub>2</sub>.

In opposition with this sample, the Ni/La<sub>2</sub>O<sub>3</sub> – Al<sub>2</sub>O<sub>3</sub> XRD patterns contain only Ni diffraction lines and no peak that could be attributed to lanthanum oxide. This behavior of lanthana containing alumina supported nickel catalysts was previously reported<sup>5, 6</sup> and indicates either a high dispersion of lanthanum oxide or the prevalence of the oxide in amorphous phase. In the XRD pattern of La<sub>2</sub>O<sub>3</sub> – Al<sub>2</sub>O<sub>3</sub> support obtained by impregnation of alumina with lanthanum nitrate followed by calcinations, the diffraction lines of lanthanum oxide are present (Fig. 2) as follows: La<sub>2</sub>O<sub>3</sub> (1 1 0) at 28.1°, La<sub>2</sub>O<sub>3</sub> (2 0 0) at 39.5°, La<sub>2</sub>O<sub>3</sub> (2 1 1) at 48.4° and La<sub>2</sub>O<sub>3</sub> (2 2 0) at 56.9°.<sup>7</sup> The absence of these lines in the Ni/La<sub>2</sub>O<sub>3</sub>–Al<sub>2</sub>O<sub>3</sub> XRD spectrum suggests that the structure and morphology of deposited La<sub>2</sub>O<sub>3</sub> on the alumina surface is changed during the catalysts preparation procedure, most probably in the hydrogen reduction step.

For all catalyst samples, the nickel crystallite size was calculated using Scherrer's equation. The results are presented in Table 1. By adding ceria to catalysts support the medium size of nickel crystallite decreases. The addition of lanthana leads to larger nickel metallic crystallites.

XPS spectroscopy was used to study the elements species which are present on the catalysts surface and their oxidation states. In all catalyst samples, nickel appears in XPS spectra in three forms: one correspond 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 energies of about 855.1 eV and about 857.2 eV. 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).<sup>8</sup> 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. 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.

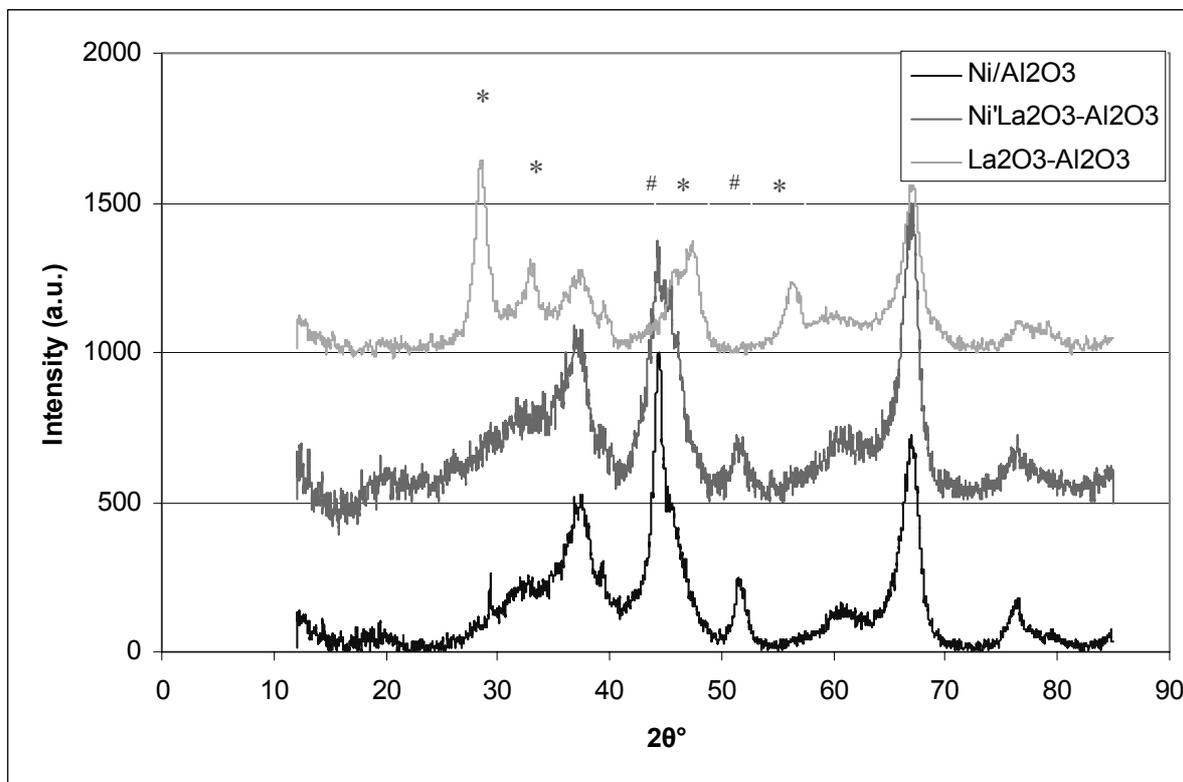


Fig. 2 – XRD pattern of lanthana modified nickel catalysts; (#) - peaks correspond to Ni; (\*) - peaks correspond to La<sub>2</sub>O<sub>3</sub>.

For Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> the peaks corresponding to cerium are in the same region of the XPS spectra as the peaks corresponding to nickel. Due to the overlapping of all these peaks it was not possible for us to extract the cerium spectra from the general spectra of the sample. It can be seen that cerium is present on the catalyst surface, due to the differences between the XPS spectra of Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> and the same region of the Ni/Al<sub>2</sub>O<sub>3</sub> spectra, showing a clear influence of cerium, but it was not possible to establish its oxidation state.

For Ni/La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> catalyst the peaks corresponding to lanthanum are present in the 830 eV – 860 eV region (Fig. 3). The La 3d electrons signal is split into its 5/2 and 3/2 components due to

electrons spin-orbit coupling. There is also some additional structure, which is due to configuration-interaction type processes. Therefore, each line is further split due to the transfer of an electron from oxygen 2p orbital to the empty lanthanum 4f shell, leading to the 4f<sup>0</sup> and 4f<sup>1</sup> final states. Furthermore, in the literature was reported that in fact the excitation spectrum recorded does not consist simply of two neighbor peaks, but corresponds to a continuous intensity distribution, reflecting the excitations of electron valence states through the whole bandwidth.<sup>9</sup> The oxidation state of lanthanum is +3 which indicates that La<sub>2</sub>O<sub>3</sub> is the additional oxide present on the catalyst support.

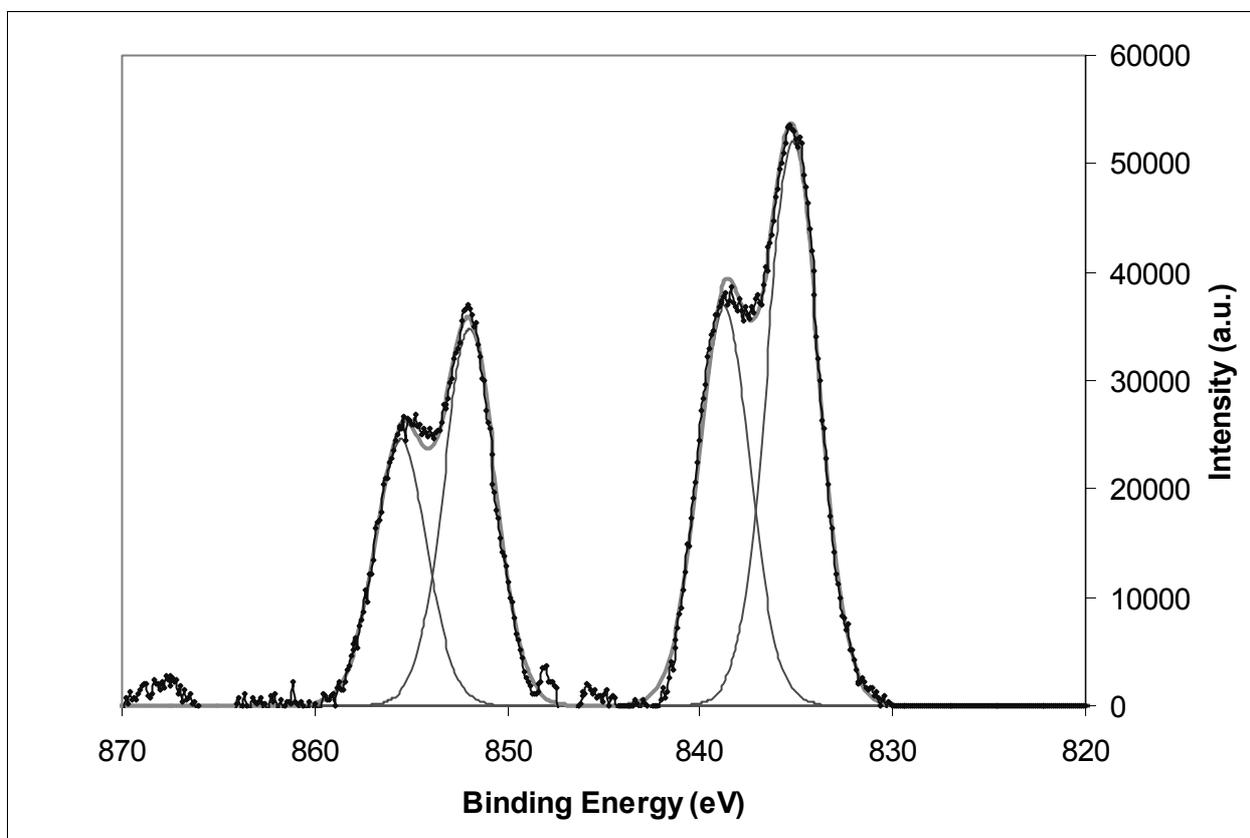


Fig. 3 – XPS spectrum of lanthanum in Ni/La<sub>2</sub>O<sub>3</sub> – Al<sub>2</sub>O<sub>3</sub> catalyst.

### Catalytic activity results

The catalysts were tested in the temperature range of 450 – 700°C. The methane flow was 35 ml/min and methane to steam (C/S) ratio was 1:4. The main products of the methane steam reforming reaction catalyzed by alumina and promoted alumina supported Ni catalysts are H<sub>2</sub> and CO<sub>2</sub>. Carbon monoxide is also present in low concentrations in the effluent gases for reactions carried out at low temperatures (T < 600°C). For

higher temperatures reaction the proportion of CO in the reaction products increases (more than 10% for 700°C) indicating a decrease in the WGS reaction rate. The addition of supplementary oxide does not significantly change the ratio between the CO and CO<sub>2</sub> in the effluent gases.

All tested catalysts present catalytic activity for methane steam reforming starting with 450°C. The methane conversion increases with temperature for all three catalysts, reaching a maximum value of almost 100% at 700°C (Fig. 4).

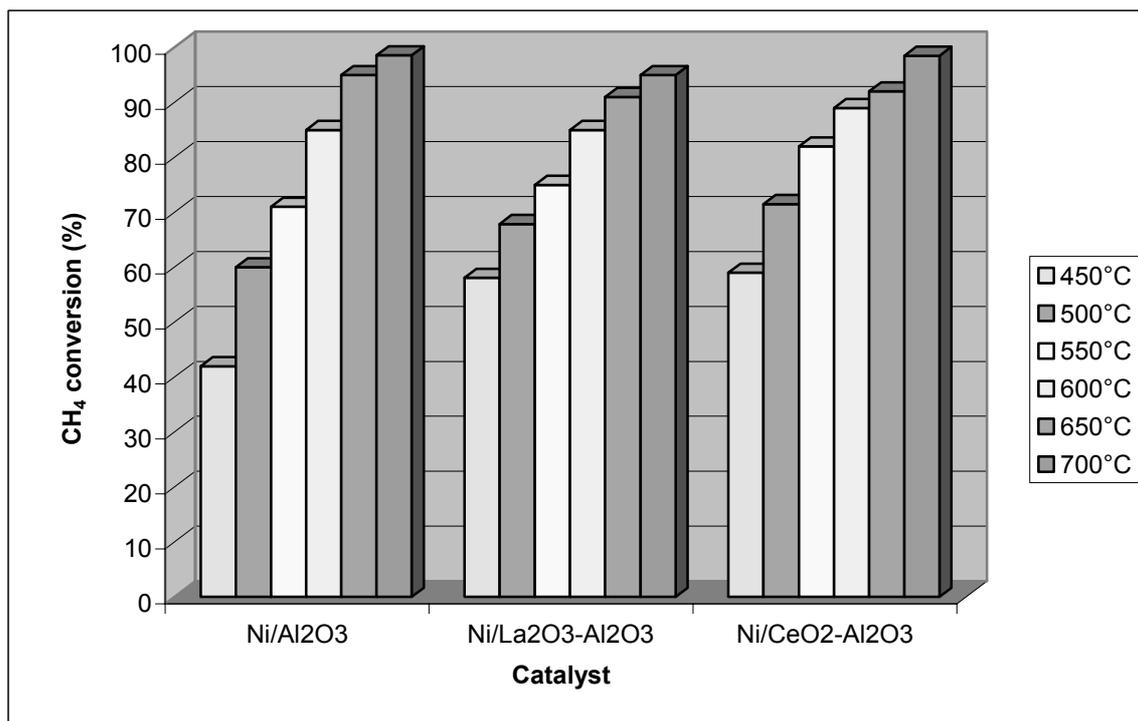


Fig. 4 – Methane conversion versus reaction temperature for oxide promoted alumina supported nickel catalyst.

The addition of CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> improves the Ni/Al<sub>2</sub>O<sub>3</sub> activity for methane steam reforming. At 550°C the methane conversion for Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> is 83% compared to 73% for Ni/Al<sub>2</sub>O<sub>3</sub>. The lanthana promoted catalysts give an intermediate value of 76% of methane converted to products. At 700°C all three catalysts behave in a similar manner, the differences between the catalytic activity of promoted and un-promoted catalysts being very small. The MSR reaction mechanism implies the reaction of adsorbed CH<sub>x</sub> (x = 0–4) species from nickel with water molecules adsorbed and activated on the oxide support. Due to their basic character, the addition of ceria and lanthana to alumina enhances the support capacity to adsorb water, and consequently favor both MSR and WGS reactions. The promoting effect of CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> addition to supported nickel catalysts for hydrocarbon steam reforming was previously explained as a synergetic effect of nickel and ceria (lanthana) with the appearance of a SMSI-like interaction between two of them.<sup>2,10</sup> The authors proposed a redox mechanism in which water is adsorbed dissociative on Ce<sup>+3</sup> ions contained on the ceria surface and the resulting oxygenated adsorbed species migrate to the metal surface and react with adsorbed CH<sub>x</sub>. Ceria was also proved to be involved in WGS reaction mechanism at low

reaction temperatures, for noble metals supported on ceria catalysts.<sup>11</sup> For Pd/CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> a mechanism was proposed, in which the oxidation of surface CeO<sub>x</sub> by H<sub>2</sub>O generates active O\* species, which migrate to the metal and react with the adsorbed carbon species, improving in this way the overall reaction rate.<sup>12</sup> A common point of all these mechanisms is the implication of Ce<sup>+3</sup>/Ce<sup>+4</sup> redox equilibrium in the catalytic mechanism. Our conclusion is that the addition of CeO<sub>2</sub> and La<sub>2</sub>O<sub>3</sub> to Ni/Al<sub>2</sub>O<sub>3</sub> catalyst modifies the support basicity and capacity to adsorb water (molecular and/or dissociative) with direct influence on the MSR and WGS rate at low temperatures. At high temperatures there are evidences that cerium oxide loses its chemisorption<sup>10</sup> and its oxygen donating<sup>11</sup> capacities, thus leading to a decrease of its implication in the catalytic mechanism. It must be also taken into account, that at high temperatures, the activation effect of Al<sub>2</sub>O<sub>3</sub> increases and become in the same range with rare earth promoted Al<sub>2</sub>O<sub>3</sub>. As a result, the methane conversion for Ni/Al<sub>2</sub>O<sub>3</sub> is comparable, even slightly higher than Ni/CeO<sub>2</sub>-Al<sub>2</sub>O<sub>3</sub> or Ni/La<sub>2</sub>O<sub>3</sub>-Al<sub>2</sub>O<sub>3</sub> conversion.

The catalysts stability against deactivation was studied by measuring the methane conversion after 48h of reaction. The results are presented in Table 2.

Table 2

The catalysts stability for methane steam reforming after 48h on stream at 550°C

Catalyst	Maximum conversion <sup>a</sup> (%)	Conversion after 48h (%)	Degree of deactivation (%)
Ni/Al <sub>2</sub> O <sub>3</sub>	73	68	10
Ni/La <sub>2</sub> O <sub>3</sub> – Al <sub>2</sub> O <sub>3</sub>	76	76	0
Ni/CeO <sub>2</sub> -Al <sub>2</sub> O <sub>3</sub>	83	83	0

<sup>a</sup> conversion after 1h

In our working conditions alumina supported nickel catalysts start to deactivate after 3h. At the end of testing period approximately 10% of the initial catalytic activity was lost, indicating a steady, long termed deactivation process. This is due mainly to carbon accumulation on the nickel surface, as indicated by previous studies of Ni catalysts in methane steam reforming.<sup>13</sup> The addition of supplementary basic oxide improves the catalyst stability at low temperatures, probably by influencing the balance between the carbon-forming and carbon-removing reactions in the catalytic mechanism. By their addition to the alumina, the support basicity is enhanced, in the same time with oxygen mobility on the surface, creating better conditions for carbon to combine with oxygen and leave the catalyst surface.

## EXPERIMENTAL

The Ni/Al<sub>2</sub>O<sub>3</sub> catalyst has been prepared by wet impregnation method. An aqueous solution obtained from Ni(NO<sub>3</sub>)<sub>2</sub> × 6H<sub>2</sub>O was used to impregnate the  $\gamma$ -alumina support (Merck, S<sub>t</sub> = 135 m<sup>2</sup>/g) followed by calcination in argon at 550°C for 3h and reduction in hydrogen at 550°C. CeO<sub>2</sub> (6% wt.) and La<sub>2</sub>O<sub>3</sub> (6% wt.) promoted alumina supports were prepared by wet impregnation of  $\gamma$ -alumina with aqueous solution of Ce(NO<sub>3</sub>)<sub>3</sub> × 6H<sub>2</sub>O or La(NO<sub>3</sub>)<sub>3</sub> × 6H<sub>2</sub>O, followed by calcination in argon at 550°C for 3h. Nickel was then added to these supports by impregnation with aqueous solution of Ni(NO<sub>3</sub>)<sub>2</sub> × 6H<sub>2</sub>O. The impregnated samples were dried, calcined and reduced as described above.

The BET surface areas and pore volumes of the catalysts were measured by N<sub>2</sub> adsorption – desorption at liquid nitrogen temperature using a Sorptomatic 1900 instrument (Thermo Electron).

Power X-ray diffraction pattern were recorded using a Bruker D8 diffractometer with CuK $\alpha$ 1 radiation.

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 of the prepared catalyst was tested in a laboratory device composed by feed section, reactor, and

analytical unit, at temperature starting from 450°C to 700°C. The set-up contains a tubular reactor made from stainless steel. The carrier gas is Ar, the total flow was 50ml/min, and the C/S (methane/steam) ratio was 1:4. The reactions were carried out under atmospheric pressure using catalyst powders (1 g; 80–100  $\mu$ m) diluted with alumina powder (1 g) of similar granulometry. The outlet gas mixture is then analyzed on-line using a gas chromatograph equipped with a sampling valve, thermal conductivity detector (TCD) and Sphercarb column. Prior reaction, the catalysts samples were activated at 400°C in H<sub>2</sub> flow at 30 ml/min for 2h.

## CONCLUSIONS

Two Ni/Al<sub>2</sub>O<sub>3</sub> (7% wt. Ni) catalysts promoted by addition of CeO<sub>2</sub> (6% wt.) and La<sub>2</sub>O<sub>3</sub> (6% wt.) to the alumina support were prepared by wet impregnation and characterized by N<sub>2</sub> adsorption desorption, XRD and XPS techniques. Structural parameters (total surface area, porosity) are not influenced by the addition of secondary oxide to the Al<sub>2</sub>O<sub>3</sub> support. XRD results reveal the presence of crystalline CeO<sub>2</sub> on the catalysts surface. Lanthanum oxide is amorphous and very well dispersed and couldn't be identified by XRD. XPS results indicate the presence of La<sup>3+</sup> on the catalyst surface. Methane conversion at low temperatures (T<600°C) is improved by the addition of ceria to alumina support due to the implication of Ce<sup>+3</sup>/Ce<sup>+4</sup> redox equilibrium in the catalytic mechanism. The addition of lanthana improves also the methane conversion, but not in such extent as the addition of ceria. The promoted catalysts are more stable toward deactivation at low temperatures than unpromoted ones. At high temperatures (T>650°C) the addition of supplementary oxides does not essentially change the Ni/Al<sub>2</sub>O<sub>3</sub> catalytic properties for methane steam reforming.

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