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Effect of Mg addition on acid-base characteristics in spinels structures †

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Abstract: Two spinels type catalysts families $Ni_{1-x}Mg_xAl_2O_4$ (x = 0.01/0.05/0.1, NiMgx) and $Mg_{1-x}Ni_xAl_2O_4$ (x = 0.05/0.1/0.2, MgNix) were synthetized to generate Ni metal particles over a basic support. These catalysts were characterized by different techniques. Pure structures were obtained with a suitable surface area. NiMgx catalysts presented the highest surface area values. These catalysts also showed a higher reducibility and, therefore, the higher Ni^0 content at the surface. The presence of basic strong sites was observed for MgNix while NiMgx only presented weak and medium basic sites, then NiMgx catalysts could be used in reactions where medium basic sites are needed.

Keywords: hydrogen; basic supports; nickel; magnesium; spinels

1. Introduction

Ethanol steam reforming (ESR) is one of the main processes to obtain H_2 as energy source. For each mole of ethanol 6 moles of H_2 are obtained:

$$CH_3CH_2OH\ (g) + 3H_2O\ (g) \rightarrow 2\ CO_2\ (g) + 6H_2\ (g) \quad (1)$$

The Ni based catalysts are the most used for ESR because they do not have high prices as the precious metals and these catalysts have a high capacity to break the C-C bond [1]. The highly stable spinels structures are widely used as support for the catalysts in ESR. In spinels structures, after the activation stage, the Ni particles migrate towards the surface, achieving a nickel-aluminum oxide catalyst with a great interaction of the particles with the support, so the support plays a fundamental role. Acidic supports, such as alumina, favor dehydration reactions that produce ethylene as an intermediate product. Ethylene is easily transformed into carbon thus causing the poisoning of the catalyst. It has been suggested that the addition of alkaline elements (K, Mg, Ca) neutralizes acidic sites and reduces carbon formation by suppressing cracking and polymerization reactions, improving catalyst stability [2]. One of the most studied structure is the $MgAl_2O_4$ which also has high thermal stability [3,4].

The aim of this work is to generate Ni particles from a defined spinel-like structure and to study the properties of the catalysts in order to determine if they are appropriate for their subsequent use in the ESR reaction.

2. Materials and methods

The spinels type catalysts families $Ni_{1-x}Mg_xAl_2O_4$ (x = 0.01/0.05/0.1, NiMgx) and $Mg_{1-x}Ni_xAl_2O_4$ (x = 0.05/0.1/0.2, MgNix) were synthetized by the citrate method [5]. These catalysts were characterized by different techniques such as X-ray diffraction (XRD), specific surface area (S_{BET}), temperature programed reduction (TPR), temperature programed desorption of CO_2 (TPD-CO2) and x-ray photoelectron spectroscopy (XPS).

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3. Result and discussion

As previously stated, the spinel-like solids were synthesized by the citrate method. This method is known for providing high purity solids with suitable specific surfaces to be used as catalysts. The purity of the materials was verified by XRD studies, figure 1.

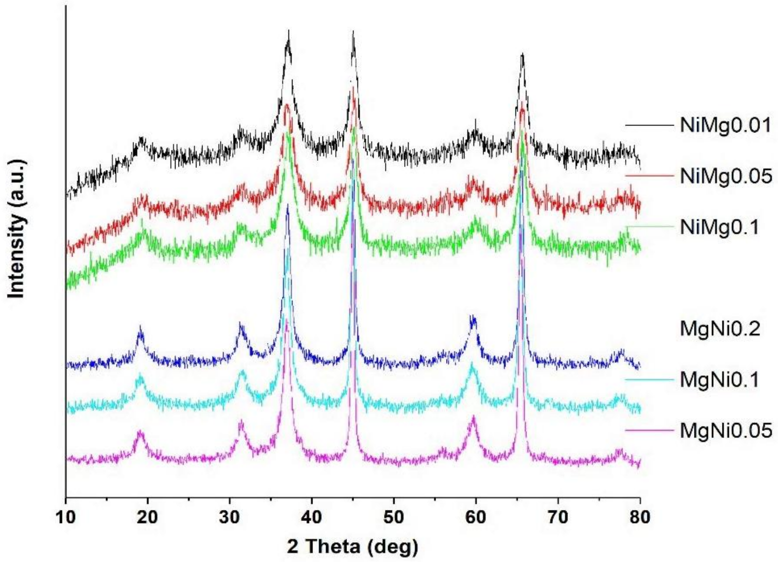


Figure 1. XRD of catalysts.

For the NiMgx family only the phase $NiAl_2O_4$ (96-900-1439) was identified. $MgAl_2O_4$ (96-900-5810) phase was observed for MgNix family. In the case of $NiMg_{0.1}$ spinel, a signal corresponding to MgO (96-900-6748) was also observed with the presence of the peaks $2\theta = 42.97$ and 62.39 °. The MgNix spinels presented patterns with the lower noise. Low noise is characteristic of solids with a larger crystallite size, as it can observe in the table 1. The sizes were determined using the Scherrer equation.

Table 1. Crystallite size, S_{BET}, contribution area (%) of catalysts from TPD-CO_2 results and Ni^0 contribution from XPS.

Catalyst	Crystallite size (Å)	S_{BET} (m^2g^{-1})	(% area) Range 110 - 120 °C	(% area) Range 150 - 185 °C	(% area) Range 225 - 275 °C	Contribution of Ni^0 (%)
$NiMg_{0.01}$	84	87	49.06	50.94	-	6.44
$NiMg_{0.05}$	82	82	62.33	37.67	-	5.60
$NiMg_{0.1}$	87	75	63.36	36.64	-	6.10
$MgNi_{0.05}$	183	44	54.68	26.6	18.72	3.70
$MgNi_{0.1}$	201	26	45.60	38.19	16.13	3.21
$MgNi_{0.2}$	239	26	40.68	35.42	23.9	2.31

Table 1 shows that $NiMg_{0.01}$, $NiMg_{0.05}$ and $NiMg_{0.1}$ catalysts presented a greater surface area with values between 75 and 87 m^2g^{-1} than $MgNi_{0.05}$, $MgNi_{0.1}$ and $MgNi_{0.2}$ catalysts, which presented values between 26 and 44 m^2g^{-1}. In addition, it was observed a decrease of surface area with the increase of Mg content for all synthetized materials.

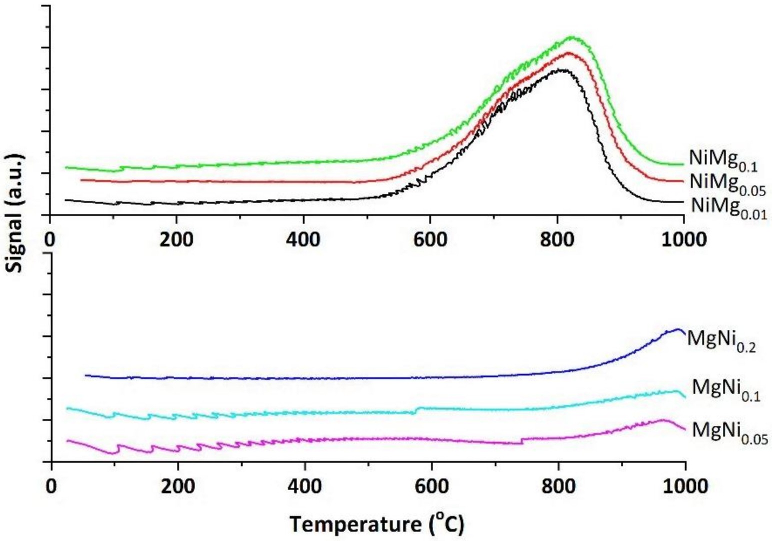
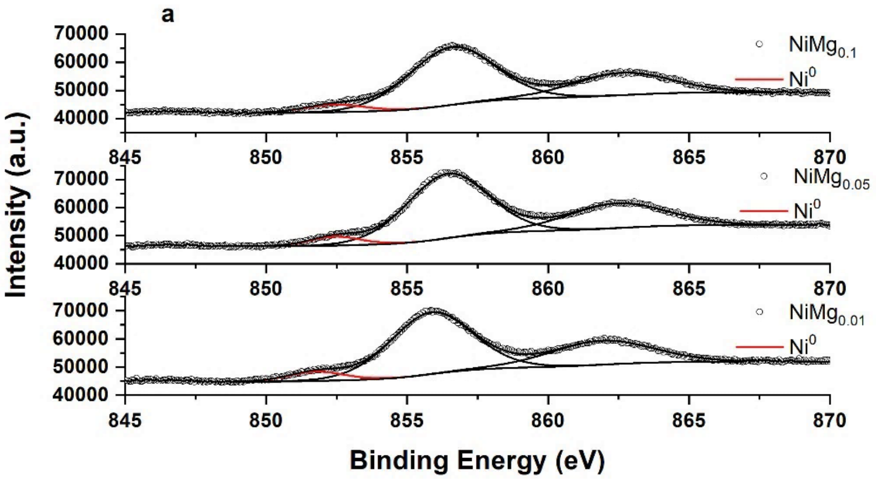


Figure 2. TPR profiles of catalysts.

The purity of these materials can be also analyzed from TPR results. This technique is also usefull to know the nature of Ni metallic particles generated. The reduction profiles of all materials are shown in figure 2. All the spinels had a main reduction signal, which would correspond to the Ni reduction from the spinel structure [6]. Ni reduction signals presented a maximum value around 800 and 840 °C for $NiMg_{0.01}$, $NiMg_{0.05}$ and $NiMg_{0.1}$. These signals also present shoulders which could indicate the presence of Ni outside the spinel structure but with a high interaction with the support. Dieuzeide et al [6] reported reduction signals above 750 °C corresponding to the reduction of Ni from the $NiAl_2O_4$ spinel. The reducibility of Ni in $MgNi_{0.05}$, $MgNi_{0.1}$ and $MgNi_{0.2}$ spinels is lower, as it can be observed a small reduction signal could be detected at almost at 1000 °C. In general, the maximum temperature of reduction increases slightly with the increase of Mg content. By this way, it is demonstrated that the increase of Mg in the structures increases the material stability as reported by Jang et al [7].



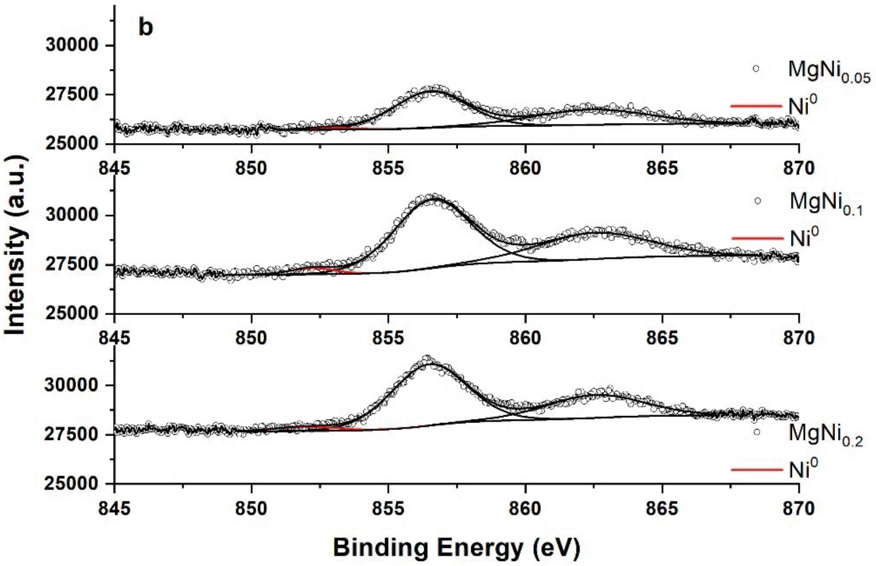
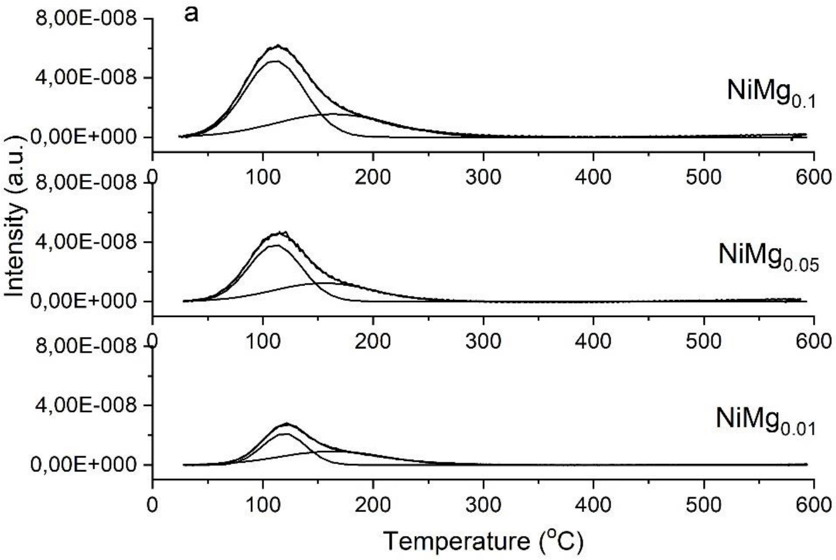


Figure 3. Ni2p3/2 spectra of catalysts.

Figures 3a and 3b show the Ni2p3/2 spectra of the materials previously reduced at 500 °C for 1 h in a mixture of H_2/N_2 (5 %). Three components were determined from the Ni2p3/2 signal. The main signal at 856 eV was attributed to Ni from the spinel or NiO species. A Ni satellite peak at 861 eV as also detected. $NiMg_{0.01}$, $NiMg_{0.05}$ and $NiMg_{0.1}$ clearly showed the presence of a peak at 852 eV corresponding to surface Ni^0 [8–10]. This signal is less intense for MgNix catalysts but a small shoulder can be noticed at this binding energy. Table 1 presented the contribution of Ni^0 in the Ni2p3/2 signal. It can be seen that a higher contribution of Ni^0 was found in NiMgx than in MgNix spinels. These results indicate a lower reducibility of the Ni species in the MgNix catalyst as observed by TPR, which could affect the efficiency of this catalyst in ESR reaction.



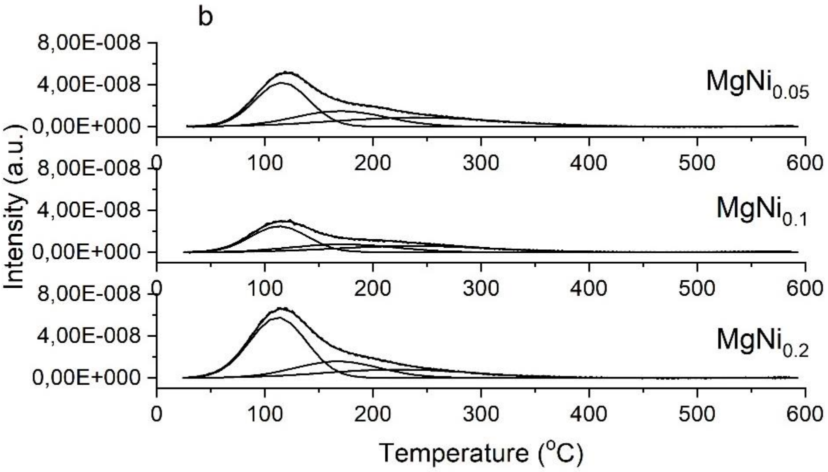


Figure 4. DTP-CO_2 of catalysts.

As it was mentioned above, one of the precursors of carbon is ethylene, which is produced by the presence of acidic sites on the catalyst. For this reason, it was decided to study the incorporation of a basic cation, Mg, in the different synthesized solids. The basicity of the materials was determined by DTP-CO_2, figures 4a and 4b. CO_2 desorption signals of NiMgx spinels could be deconvoluted into two peaks in the temperature ranges of 110 - 120 °C and 150 - 185 °C corresponding to weak and moderate basic sites respectively. MgNix spinels presented, in addition to those signals, the contribution of another signal in the temperature range of 225-275 °C, demonstrating the existence of strong basic sites on surface [11,12]. Table 1 shows the area (%) that represents the contribution of the signal from each temperature range to the overall signal for each compound. In general, it is evident that the basic properties of catalysts increased as the Mg content of in the compounds increased.

Although the MgNix is the family that presents strong basic sites, NiMgx has moderate basic sites in addition to the weak sites. In general, it is evident that as the content of Mg in the compounds increases, the basic properties are also increased. The results obtained in this work, are in concordance with the study carried out by Di Cosimo et al [11]. In addition, NiMgx family presented higher surface areas, better Ni reducibility and therefore a greater amount of surface Ni^0. According to the results obtained in this work, it could be assumed that the NiMgx family catalysts would be more suitable to be used in ESR

4. Conclusions

Ni particles were generated after a reduction step from high purity solids with a defined spinel-like structure. Pure structures were obtained in all cases with a suitable surface area. NiMgx catalysts presented the highest surface area values. These catalysts also showed a higher reducibility and, therefore, the higher metallic Ni content at the surface. The presence of basic strong sites was observed for MgNix while NiMgx only presented weak and medium basic sites, then NiMgx catalysts could be used in ESR.

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References

1. Morales-Marín, A.; Ayastuy, J.L.; Iriarte-Velasco, U.; Gutiérrez-Ortiz, M.A. Nickel Aluminate Spinel-Derived Catalysts for the Aqueous Phase Reforming of Glycerol: Effect of Reduction Temperature. *Appl. Catal. B Environ.* **2019**, *244*, 931–945.
2. Vizcaíno, A.J.; Arena, P.; Baronetti, G.; Carrero, A.; Calles, J.A.; Laborde, M.A.; Amadeo, N. Ethanol Steam Reforming on Ni/Al2O3 Catalysts: Effect of Mg Addition. *Int. J. Hydrogen Energy* **2008**, *33*, 3489–3492.
3. Habibi, N.; Wang, Y.; Arandiyan, H.; Rezaei, M. Effect of Substitution by Ni in MgAl2O4 Spinel for Biogas Dry Reforming. *Int. J. Hydrogen Energy* **2017**, *42*, 24159–24168.
4. Habibi, N.; Wang, Y.; Arandiyan, H.; Rezaei, M. Low-Temperature Synthesis of Mesoporous Nanocrystalline Magnesium Aluminate (MgAl2O4) Spinel with High Surface Area Using a Novel Modified Sol-Gel Method. *Adv. Powder Technol.* **2017**, *28*, 1249–1257.
5. Courty, P.; Ajot, H.; Marcilly, C.; Delmon, B. Oxydes Mixtes Ou En Solution Solide Sous Forme Très Divisée Obtenus Par Décomposition Thermique de Précurseurs Amorphes. *Powder Technol.* **1973**, *7*, 21–38, doi:https://doi.org/10.1016/0032-5910(73)80005-1.
6. Dieuzeide, M.L.; Laborde, M.; Amadeo, N.; Cannilla, C.; Bonura, G.; Frusteri, F. Hydrogen Production by Glycerol Steam Reforming: How Mg Doping Affects the Catalytic Behaviour of Ni/Al2O3 Catalysts. *Int. J. Hydrogen Energy* **2016**, *41*, 157–166.
7. Jang, W.-J.; Jung, Y.-S.; Shim, J.-O.; Roh, H.-S.; Yoon, W.L. Preparation of a Ni-MgO-Al2O3 Catalyst with High Activity and Resistance to Potassium Poisoning during Direct Internal Reforming of Methane in Molten Carbonate Fuel Cells. *J. Power Sources* **2018**, *378*, 597–602.
8. Ertl, G.; Hierl, R.; Knözinger, H.; Thiele, N.; Urbach, H.P. XPS Study of Copper Aluminate Catalysts. *Appl. Surf. Sci.* **1980**, *5*, 49–64, doi:https://doi.org/10.1016/0378-5963(80)90117-8.
9. Mandale, A.B.; Badrinarayanan, S.; Date, S.K.; Sinha, A.P.B. Photoelectron-Spectroscopic Study of Nickel, Manganese and Cobalt Selenides. *J. Electron Spectros. Relat. Phenomena* **1984**, *33*, 61–72, doi:https://doi.org/10.1016/0368-2048(84)80006-7.
10. Shang, Z.; Li, S.; Li, L.; Liu, G.; Liang, X. Highly Active and Stable Alumina Supported Nickel Nanoparticle Catalysts for Dry Reforming of Methane. *Appl. Catal. B Environ.* **2017**, *201*, 302–309, doi:https://doi.org/10.1016/j.apcatb.2016.08.019.
11. Di Cosimo, J.I.; Díez, V.K.; Xu, M.; Iglesia, E.; Apesteguía, C.R. Structure and Surface and Catalytic Properties of Mg-Al Basic Oxides. *J. Catal.* **1998**, *178*, 499–510, doi:https://doi.org/10.1006/jcat.1998.2161.
12. Hadian, N.; Rezaei, M.; Mosayebi, Z.; Meshkani, F. CO2 Reforming of Methane over Nickel Catalysts Supported on Nanocrystalline MgAl2O4 with High Surface Area. *J. Nat. Gas Chem.* **2012**, *21*, 200–206, doi:https://doi.org/10.1016/S1003-9953(11)60355-1.