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## Glycerol conversion into H<sub>2</sub> by steam reforming over Ni and PtNi catalysts supported on MgO modified $\gamma$ -Al<sub>2</sub>O<sub>3</sub>

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### Abstract

The glycerol catalytic steam reforming over Ni and PtNi catalysts to produce H<sub>2</sub> was studied. The activity results indicate that the catalyst with the lower content of MgO, the NiA1M, provides higher H<sub>2</sub> molar ratios than the Ni catalyst. The behaviour of the NiA1M catalysts seems to be related to the Ni<sup>0</sup> species stabilization by nickel-magnesia interactions, which are favoured by the presence of well dispersed MgAl<sub>2</sub>O<sub>4</sub> spinels. The bimetallic catalyst, PtNiA3M named, reforms the intermediate products improving the activity of the Ni monometallic catalyst toward H<sub>2</sub> production. The characterization results suggest that the Pt in the Ni monometallic catalyst enhances the Ni<sup>0</sup> particles dispersion and the nickel species reducibility by H<sub>2</sub> spillover.

**Keywords:** glycerol, hydrogen, nickel, platinum, magnesia

### 1. Introduction

In the last years, the attention has been focused on the H<sub>2</sub> potential as clean energy vector. Moreover, this energy vector could be more attractive if it is produced from biomass-derived products such as glycerol. Glycerol, the main by-product in the biodiesel production, can be revalorised by its conversion into H<sub>2</sub> using catalytic steam reforming. In this way, the impact on the total biodiesel manufacturing cost will be also reduced by valorization of this by-product [1]. The hydrocarbons steam reforming (SR) uses Al<sub>2</sub>O<sub>3</sub>-supported Ni catalysts [2] because these systems are more inexpensive than noble catalysts in industrial applications [3]. However, these catalytic systems suffer deactivation due to coke formation and/or metallic phase sintering related to the low thermal resistance of Al<sub>2</sub>O<sub>3</sub>. To improve the properties of this kind of catalysts and avoid its deactivation, the support can be modified with MgO.

### 2. Catalysts and reaction conditions

#### 2.1. Materials and Methods

The modified  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> supports were impregnated with different amounts of Mg(NO<sub>3</sub>)<sub>2</sub> aqueous solutions and then were dried and calcined. Afterwards, the Ni was added to the supports by impregnation, drying and calcination, obtaining the catalysts designated as NiA1M, NiA3M, NiA15M, NiM and NiA. The bimetallic catalyst, PtNiA3M, was prepared by impregnation of the NiA3M catalysts with Pt, following by a drying and calcination. The theoretical Ni and Pt content was around 13 and 2.6 wt%, respectively.

The activity tests were carried out in fixed bed continuous catalytic reactor in which 200 mg of catalyst (0.42-0.5 mm) was diluted with inert CSi (1:9 wt). Prior to reaction, the catalysts were activated in situ with 75 mL<sub>(STP)</sub>/min of pure H<sub>2</sub> at 0.1 MPa and 973 K during 2h. The reduced catalysts were tested under a space velocity of 7.7 g<sub>glycerol</sub>/g<sub>catalyst</sub>h, 0.4 MPa of total pressure and temperatures of 773 K and 873 K using 10 wt% glycerol diluted in water as a feed stock. Gas chromatography was used to determine the type and amounts of reaction products.

## 2.2. Characterization techniques

The calcined and reduced catalysts were characterized by temperature-programmed reduction (TPR), x-ray powder diffraction (XRD) and x-ray photoelectron spectroscopy (XPS). The reduction treatment to the catalysts was carried out ex-situ at 923 K under 100 mL/min of H<sub>2</sub>/N<sub>2</sub> (1/9) gas mixture. For the XPS characterization is used a second reduction treatment in-situ under the same gas mixture flow and at 773 K.

The TPR experiments were carried out with semiautomatic Micromeritics TPD/TPR 2900 apparatus equipped with a TCD detector. The TPR profiles were obtained by heating the samples from 298 to 1173 K. The XRD patterns were obtained with a computerised Seifert XRD 3000P vertical diffractometer (Cu K $\alpha$  radiation,  $\lambda=0.15418$  nm) equipped with a PW Bragg-Brentano  $\theta/2\theta$  goniometer. The samples were scanned with Bragg's angles between 5° and 80°. X-ray photoelectron spectroscopy (XPS) data were obtained using a VG Escalab 200R electron spectrometer equipped with a Mg K $\alpha$  X-ray source and a hemispherical electron analyser.

## 3. Experimental results and discussion

### 3.1. Characterization

The TPR profiles for calcined Ni and PtNi catalysts are presented in the Fig 1. The NiM catalyst profile shows two reduction peaks at 524 and 670 K associated to isolated NiO [4] and NiO interacting with the MgO respectively. The profiles of the NiA, NiA1M, NiA3M and NiA15M catalysts show a contribution of three peaks attributed to the reduction of NiO weakly interacting with the Al<sub>2</sub>O<sub>3</sub>, NiO-Al<sub>2</sub>O<sub>3</sub>, to the non-stoichiometric Ni aluminate species, NiAl<sub>x</sub>O<sub>y</sub>, and to the stoichiometric NiAl<sub>2</sub>O<sub>4</sub> species [5] respectively.

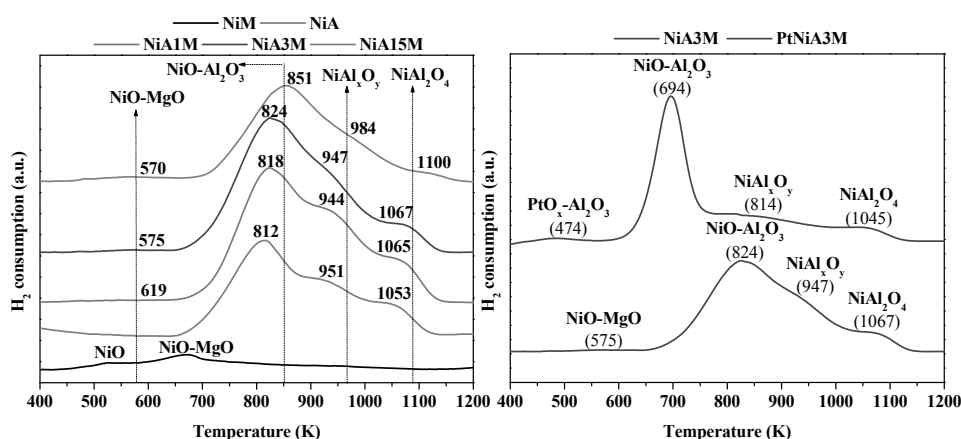


Figure 1. Reducibility profiles of calcined catalysts obtained from TPR.

The NiA1M, NiA3M and NiA15M catalysts show additional peak ascribed to NiO interacting with the MgO. The PtNiA3M catalyst shows the same Ni<sup>2+</sup> reducible species than the NiA3M catalyst. Nevertheless, the reduction temperatures decrease and the NiO-Al<sub>2</sub>O<sub>3</sub> species contribution increases. These phenomena can be due to the H<sub>2</sub> spillover generated by the Pt presence [6].

The XRD analysis was used to determinate the average particle size of Ni<sup>0</sup> species on reduced catalysts. The average particle size of crystalline Ni<sup>0</sup> species shown in the Table 1 was calculated using the Debye-Scherrer equation. The NiAM, NiA1M, NiA3M and NiA15M catalysts present Ni<sup>0</sup> particle diameters very similar. The Ni<sup>0</sup> particles size for the PtNiA3M catalyst is slightly higher than for NiA3M catalyst.

As it is observed in the Table 1, the difference between surface atomic Mg/Al ratio of calcined and reduced catalysts is lower for the NiA1M catalyst than for the NiA3M and NiA15M catalysts. This observation suggests that the MgAl<sub>2</sub>O<sub>4</sub> species (50.2 eV [7]), are better dispersed in the NiA1M catalyst. The good surface dispersion of MgAl<sub>2</sub>O<sub>4</sub> species could hinder the surface Ni<sup>0</sup> species diffusion on the alumina [7] and favouring the stabilization of Ni<sup>0</sup> by the interaction with the magnesia. Hence, the binding energy showed by Ni<sup>0</sup> in the NiA1M catalysts is similar to the NiM catalyst and higher than the NiA3M and NiA15M catalysts. The value of 48.7 eV is ascribed to surface MgO species [8].

Table 1. Different parameters determined by XPS and XRD for reduced catalysts.

Catalysts	XPS						XRD
	Ni2p <sub>3/2</sub> (eV)		Pt 4d <sub>5/2</sub> (eV)	Mg2p (eV)	Mg/Al	Ni/Al	Ni (nm)
	Ni <sup>2+</sup>	Ni <sup>0</sup>	Pt <sup>0</sup>				
NiA	856.4	852.7	-	-	-	0.03 (0.11) <sup>a</sup>	-
NiM	856.3	852.3	-	48.7	-	-	7
NiA1M	856.4	852.3	-	50.1	0.03 (0.02) <sup>a</sup>	0.02 (0.17) <sup>a</sup>	7
NiA3M	856.4	851.4	-	50.4	0.04 (0.05) <sup>a</sup>	0.02 (0.17) <sup>a</sup>	7
NiA15M	856.3	851.3	-	49.4	0.18 (0.24) <sup>a</sup>	0.02 (0.20) <sup>a</sup>	6
PtNiA3M	856.1	852.8	314.3	50.2	0.02 (0.02) <sup>a</sup>	0.02 (0.11) <sup>a</sup>	5

(a → data for calcined catalysts)

### 3.2. Catalytic Activity

The glycerol conversion and the SR gas products molar ratios are shown in Figure 2A. All the catalysts provide the total glycerol conversion at 773 K, except the NiM catalyst. This suggests that the  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> support plays an important role in the glycerol conversion. Moreover, the H<sub>2</sub> and the CO<sub>2</sub> are produced as the main components of the gas when the catalysts supported on bare and MgO-modified Al<sub>2</sub>O<sub>3</sub> are used. Regarding H<sub>2</sub> molar ratio obtained with NiA, NiA1M, NiA3M and NiA15M, it can be observed that this ratio increases when NiA1M is used. When the MgO load is increased from 1M to 15M the H<sub>2</sub> ratio decreases indicating that higher amounts of modifier are not effective to improve the H<sub>2</sub> production. The low H<sub>2</sub> production obtained with NiA, NiA3M and NiA15M is related to the higher formation of oxygenated hydrocarbons (OHC-s) which are collected in the liquid phase. The OHC-s are mainly acetaldehyde, acrolein, propionaldehyde and acetone. All the OCH-s are included as C wt% (OHC-s total amount in liquid phase given in dry basis) in the Figure 2B and they are mainly produced through dehydration/hydrogenation reactions in which the H<sub>2</sub> is consumed.

The different behaviour of the MgO-modified Ni catalysts seems to be related to the interaction between surface Ni metallic particles and the MgO. As it has been indicate the low amounts of MgO provokes a better stabilization of surface Ni metallic particles favoured by the well dispersed MgAl<sub>2</sub>O<sub>4</sub> species. In the case of the NiA3M and

NiA15M catalysts specially, the Ni<sup>0</sup>-MgO interactions are weakened. This phenomenon could favour the formation of nickel-alumina interactions which could be promote by lower dispersion of MgAl<sub>2</sub>O<sub>3</sub>. The formation of nickel-alumina interactions could provide a similar activity for the NiA3M catalyst and lower activity for the NiA15M catalyst than the NiA catalyst.

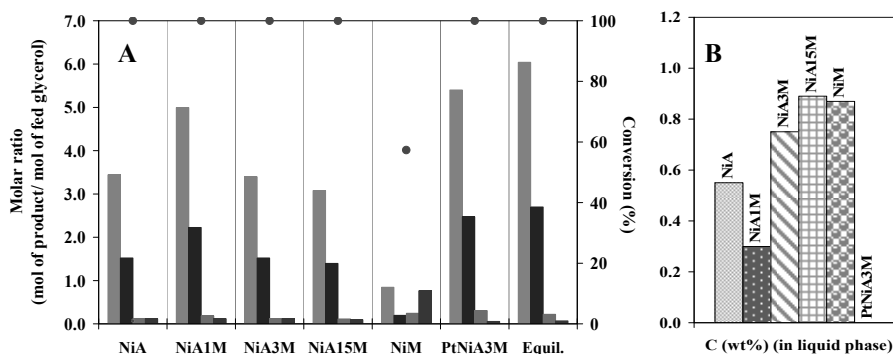


Figure 2. (A) Gas products molar ratios and conversion (■H<sub>2</sub>, ■CO<sub>2</sub>, ■CH<sub>4</sub>, ■CO, ●conversion), and (B) OHC-s amount in liquid phase given as C(wt%) in dry basis at steady state and 773 K.

The H<sub>2</sub> production increases when Pt is added to NiA3M due to the bimetallic catalyst ability to transform OHC-s into H<sub>2</sub>, CO<sub>2</sub>, CH<sub>4</sub> and CO. This behaviour could be associated to the Ni<sup>0</sup> species dispersion determined by DRX, which is slightly higher than in the NiA3M catalysts, besides the metallic phases combination, where Pt promotes the H<sub>2</sub> spillover increasing the reducibility of Ni species observed by TPR.

After the measurements at 773 K, the catalysts were tested at 873 K. The results indicated that all the catalysts, except the NiM, were able to convert completely glycerol and OHC-s achieving activity data closed to the thermodynamic equilibrium. For NiM catalysts, the measured conversion and C wt% were 41.3% and 1.3 % respectively.

#### 4. Conclusions

The main conclusions of this study are: (a) the total glycerol conversion is obtained with catalyst supported on bare and Mg-modified Al<sub>2</sub>O<sub>3</sub>, (b) the formation of OHC-s liquid products has influence on H<sub>2</sub> production, (c) low amounts of MgO are effective to improve H<sub>2</sub> ratio due to surface Ni<sup>0</sup> species stabilization (d) the Pt addition on Ni catalyst promotes the OHC-s transformation into H<sub>2</sub> due to Pt favours Ni<sup>0</sup> dispersion.

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