Catalysis Today 172 (2011) 183–188

Contents lists available at ScienceDirect

Catalysis Today

journal homepage: www.elsevier.com/locate/cattod

Hydrogen production by glycerol steam reforming with Pt/SiO_2 and Ni/SiO_2 catalysts

Francisco Pompeo, Gerardo F. Santori, Nora N. Nichio*

Facultad de Ingeniería, PIDCAT, CINDECA, Facultad de Ciencias Exactas, Universidad Nacional de La Plata, CCT La Plata-CONICET, 47 N° 257, 1 esq. 47, 1900 La Plata, Argentina

ARTICLE INFO

Article history:
Received 23 November 2010
Received in revised form 15 April 2011
Accepted 2 May 2011
Available online 1 June 2011

Keywords:
Hydrogen
Glycerol
Steam reforming
Platinum
Nickel

ABSTRACT

Pt and Ni catalysts supported on SiO_2 were prepared with different metal content in order to apply them in steam reforming of glycerol at temperatures between 350 °C and 450 °C.

Conditions of temperature and space time (τ) that can provide the total conversion of glycerol to gaseous products were found.

Based on the identification of liquids or reaction intermediates, we found that Ni and Pt have the same reaction steps. Thus, a schematic representation of reaction pathways was proposed involving successive steps of dehydrogenation and C–C bond cleavage, leading to H_2 and CO.

The different levels of conversion, selectivity and stability of catalysts were analyzed. Pt catalysts were more active and stable than Ni catalysts. Ni catalysts showed differences in the selectivity to gaseous products due to the increased contribution of the WGS reaction.

The Pt catalysts have shown a total conversion to gaseous products at 450 °C, without deactivation during the 40 reaction hours.

1. Introduction

H_2 production from renewable sources such as biomass has an important effect on the environment. Among the various renewable feedstock sources, glycerol is an alternative because it has relatively high hydrogen content, it is non toxic, and its storage and handling is safe. Glycerol is mainly produced as a byproduct of biodiesel production, but it can also come from the fermentation of sugars or the conversion of lignocellulose.

Some processes of H_2 production from glycerol are currently under study as the steam reforming, the aqueous phase reforming and the partial oxidation or autothermal reforming [1–14].

The steam reforming is one of the most used reactions in the hydrogen production. This process is highly endothermic and the low pressure favors the selectivity to hydrogen. The main reactions can be represented in Eqs. (1)–(4)

$$C_3H_8O_3 \overset{H_2O}{\longleftrightarrow} 3CO + 4H_2 \quad \text{(glycerol decomposition)} \qquad (1)$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \text{(water–gas shift reaction)} \qquad (2)$$

$$C_3H_8O_3 + 3H_2O \leftrightarrow 3CO_2 + 7H_2 \quad \text{(steam reforming of glycerol)} \qquad (3)$$

$$CO + 3H_2 \leftrightarrow CH_4 + H_2O \quad \text{(methanation reaction)} \qquad (4)$$

Metals that can be used as catalysts for this reaction are those ones with the ability to cleavage of C–C, O–H and C–H bonds of the molecule to be reformed. Thus, they are reported in literature as catalysts based on Pt, Ni, Ru, Re, Rh, Ir, Co and Pd. Ni is one of the most investigated metals due to its lower cost, despite the results indicating that Pt, Ru, Ir and Rh are more active [1–7].

In our early studies on this issue, we evaluated the performance of Ni catalysts supported on α-Al_2O_3 and α-Al_2O_3 modified by Ce and Zr, at temperatures above 600 °C. The most stable system resulted to be $Ni/CeO_2/\alpha$-Al_2O_3. These results were explained due to the Ce effect in inhibition of side reactions forming unsaturated hydrocarbons that are coke precursors [15].

The challenge is to find active, selective and stable catalysts for steam reforming of glycerol at low temperature, which would permit to reduce the energetic consumption. Thus, this process would have lower energy consumption than conventional gasification (550–750 °C). In this sense, Kunkes et al. reported excellent results for Pt/C, PtRe/C and PtRu/C catalysts for this reaction at 275–350 °C [6].

In previous work, we studied different platinum catalysts (1 wt%) prepared by different methods and using various supports

---

* Corresponding author.
E-mail address: nnichio@quimica.unlp.edu.ar (N.N. Nichio).

0920-5861/$ – see front matter © 2011 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2011.05.001

Table 1
Characterization results: TEM, TPR and H_2 chemisorption.

Catalyst	TEM d_{va} (nm)	TPR Temperature (°C)		TPR Reducibility[b]	H_2 chemisorption H/Me ratio (Me = Pt, Ni)
		LT[a]	HT[a]		
1Pt	2.4	110	410	0.9	0.6
2Pt	2.2	155	410	0.9	0.6
2Ni	3.0	350	470–600	0.9	0.2
5Ni	4.0	337	475–590	0.8	0.1
2Ni0.5Pt	3.5	285	457–573	0.9	0.1

[a] LT: low temperature peak, HT: high temperature peak.
[b] Reducibility: [(H_2 amount consumed by TPR)/(theoretical amount of H_2 consumption for total reduction)].

such as SiO_2, γ-Al_2O_3, ZrO_2, CeO_2–ZrO_2, which were active in the range of 350–450 °C. It was shown that the neutral character of the SiO_2 has no effect on side reactions. So Pt/SiO_2, which was prepared by ion exchange, shows a high metal dispersion, the highest activity level to gaseous products, and high selectivity to H_2 with good stability [16].

In this work, a comparative study of Ni and Pt catalysts supported on SiO_2 was carried out. The aim of this study was to obtain catalysts with metal content higher than 1 wt%, using the ion exchange method to analyze the structural characteristics and their effects on the main and side reactions in the steam reforming. A Ni–Pt bimetallic system was also studied. Finally, we analyzed the post-reaction samples by TPO/TGA in order to determine the influence of carbon deposition on catalyst deactivation.

2. Experimental

The Pt and Ni catalysts were prepared at room temperature by ionic exchange method, with an aqueous solution of $[Pt(NH_3)_4]Cl_2$ and $[Ni(NH_3)_6](NO_3)_2$, respectively. A Degussa silica (Aerosil 200, 200 $m^2\,g^{-1}$) was used as support. The ionic exchange isotherms of Pt and Ni on SiO_2 were performed in order to determine the maximum exchange capacity of the support with each precursor. The maximum metal content obtained was 2 wt% for Pt and 5 wt% for Ni. Catalysts were prepared with 1 and 2 wt% of Pt (denoted as 1Pt and 2Pt), and 2 and 5 wt% of Ni (denoted as 2Ni and 5Ni). The bimetallic catalyst 2Ni0.5Pt was obtained exchanging first Ni and then Pt, in order to obtain 2 wt% of Ni and 0.5 wt% of Pt.

Temperature programmed reduction (TPR) tests were carried out in a conventional dynamic equipment, with a H_2/N_2 ratio of 1/9 and heating rate 10 °C min^{-1} from room temperature up to 1000 °C.

Mean particle size was determined by TEM and obtained in a TEM JEOL 100C instrument. A graphite pattern was used for calibration. In order to estimate the average particle size, the particles were considered spherical and the diameter volume–area was calculated by using the following expression $d_{va} = \sum nidi^3/nidi^2$, where *ni* is the number of particles with diameter *di*.

Hydrogen chemisorption measurements were carried out in dynamic equipment with a TCD detector. Samples were reduced in H_2 at 500 °C and 700 °C for Pt and Ni, respectively during 1 h, cooled in H_2 up to 400 °C, flushed with Ar for 2 h at 400 °C and then cooled up to room temperature in Ar flow. Hydrogen pulses were then injected up to saturation. Dispersions were estimated from the hydrogen amount consumed, assuming an adsorption stoichiometry H/Me = 1, (Me = Pt, Ni).

The experimental equipment used for reaction tests of glycerol reforming is a fixed-bed quartz reactor (8 mm internal diameter) operated isothermally at atmospheric pressure. The Pt catalysts were reduced from room temperature up to 500 °C (10 °C min^{-1}) for 1 h while Ni catalysts were reduced to 700 °C for 4 h in H_2 flow (30 $cm^3\,min^{-1}$). The aqueous solution of glycerol (10 wt%) was injected to the reactor by a HPLC pump (Waters 590) with feed flow 0.5 $cm^3\,min^{-1}$. The evaporator is a quartz tube of 6 mm diameter filled with quartz pellets heated by an electric furnace. The nitrogen was used as carrier gas (50 $cm^3\,min^{-1}$). The space time ($[\tau]$ = min) is defined as $WHSV^{-1}$, where WHSV was calculated as grams of feed/min (N_2, H_2O and glycerol) per grams of catalyst. The space time used in this study was from 0.44 to 1.66 min varying the catalyst mass.

The equipment has two sampling ports, which allows to analyze the liquid products of the collecting flask and gaseous products.

The analysis of gaseous products was performed with a gas chromatograph Shimadzu GC-8A equipped with a column HayeSep DB 110-120 and GC/TCD detector. The liquid products were analyzed by gas chromatography with GC/FID (Chrompack) and mass spectrometry CG/MS detector (Shimadzu GCMS-QP5050A) with HP-PONA capillary column (50 m). The accuracy of the measured values was within 5% and the experiments could be reproduced with a relative error of 10%.

The glycerol conversion to gaseous products (CO, H_2, CO_2 and CH_4) is indicated as X_G and it was calculated based on the following equation:

$$X_G = \frac{\text{C moles in gas products}}{3 \times \text{glycerol moles in the feedstock}} \times 100$$

The glycerol conversion to liquid products is indicated as X_L and it was calculated based on the following equation:

$$X_L = \frac{\text{glycerol moles in the feedstock} - \text{glycerol moles in liquid products}}{\text{glycerol moles in the feedstock}} \times 100 - X_G$$

The gas product composition [% mol/mol (dry basis)] was calculated as: produced moles of H_2, CO, CO_2 and CH_4 respectively, divided total moles of gas phase × 100. The activity on time was expressed as coefficient "a_s" that expresses the ratio between gaseous glycerol conversion at time "t" divided the initial gaseous glycerol conversion.

Carbon deposits were characterized by temperature programmed oxidation (TPO), measuring the weight variation as function of the temperature in a thermogravimetric instrument (Shimadzu TGA 50). Post reaction samples of 0.008 g were used with air flow of 40 $cm^3\,min^{-1}$ and heating of 10 °C min^{-1} from room temperature to 850 °C.

3. Results and discussion

Table 1 shows catalysts studied, their nomenclature and some characterization results by TEM, TPR and H_2 chemisorption. Results of TEM measurements, also shown in histograms in Fig. 1, indicate that the particle size distribution is very narrow and centered around 2.2–4 nm.

TPR analysis showed a high reducibility in all catalysts studied, between 0.8 and 0.9. TPR profiles of Pt catalysts (Fig. 2) show the

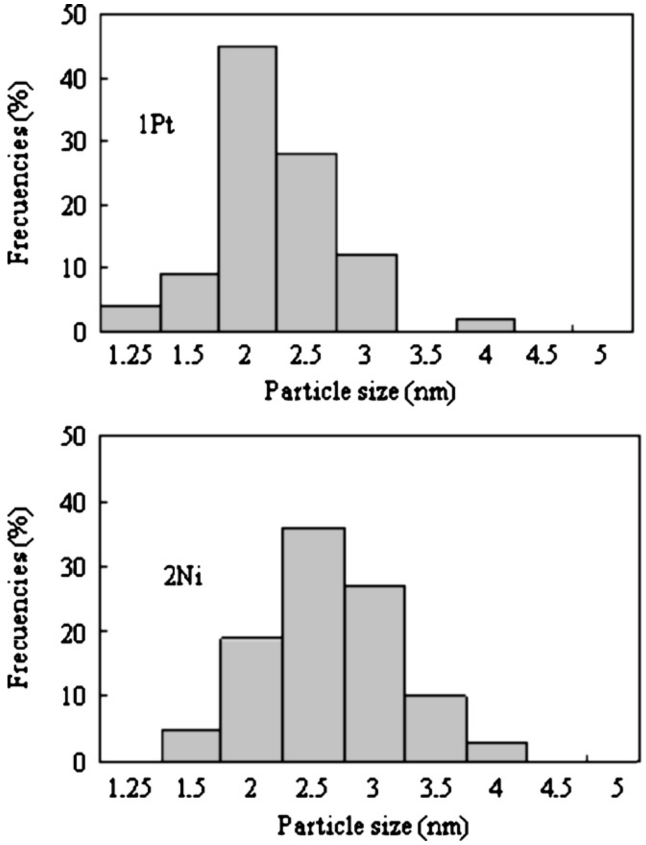

Fig. 1. Particle size distribution determined by transmission electron microscopy (TEM).

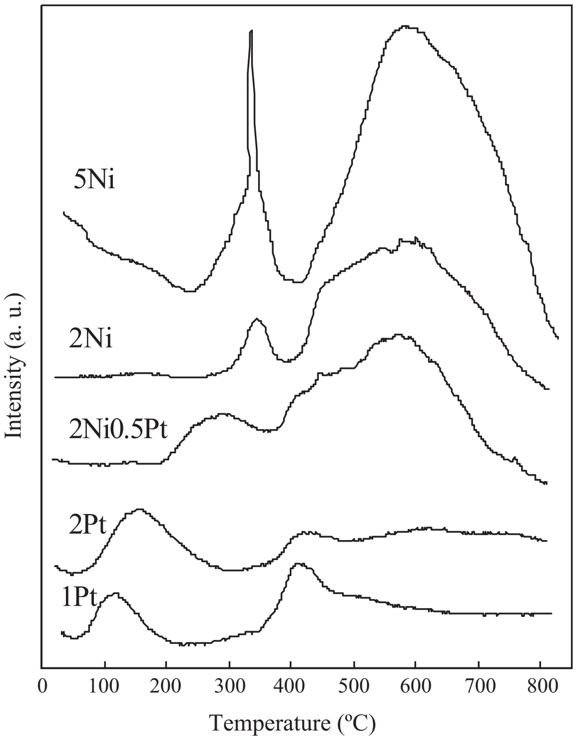

Fig. 2. Temperature programmed reduction (TPR) profiles.

existence of two main peaks of hydrogen consumption. As cited in the literature [17], this indicates the presence of two types of platinum oxides; with weak interaction with the support that reduces below 220 °C, and with strong interaction with the support when the hydrogen consumption is from 350 °C.

Regarding Ni catalysts, the profiles of the samples exhibit a very broad reduction peak between 400 °C and 800 °C. This is consistent with literature indicating that the preparation method by ion exchange leads to the formation of nickel silicates with high thermal stability [18].

The bimetallic catalyst shows that the addition of a small amount of Pt (0.5 wt%) into the Ni sample leads to a shift of the TPR peak to higher value than 1Pt. This suggests a formation of bimetallic PtNi particles. The formation of noble metal-Ni clusters in the bimetallic systems has been reported by several authors [19].

Results of hydrogen chemisorption by the pulse method showed that Pt catalysts have higher H/Pt ratio, indicating their highest metallic dispersion. 2Ni catalyst has an H/Ni ratio equal to 0.2. When Pt is added to generate the 2Ni0.5Pt bimetallic catalyst, the H/Me ratio decreases to 0.1, suggesting the strong interaction Pt–Ni due to the formation of a bimetallic phase that could modify electronically the adsorptive properties of the 2Ni catalyst.

The steam reforming of glycerol was studied under conditions indicated in Section 2. First, blank tests were performed to determine the thermal decomposition of the feed solution (10 wt% glycerol). With a support (SiO_2) at temperature range of 350–450 °C, the glycerol decomposition was less than 5% molar. The main decomposition products were acetol, 2-oxopropanal and acetaldehyde.

Catalytic activity results are shown in Table 2. In this table, the conversion to gaseous products (X_G), conversion to liquid products

Table 2
Glycerol conversion and gaseous products in the steam reforming.

Test no.	Catalyst	Temp. (°C)	τ (min)	X_{total} (%)	X_G (%)	X_L (%)	Gas product composition [% mol/mol (dry basis)]			
							H_2	CO	CH_4	CO_2
1	1Pt	350	0.44	75	46	29	59.8	38.1	1.0	1.1
2	1Pt	350	0.88	88	85	3	57.2	40.4	1.2	1.2
3	1Pt	350	1.66	100	100	0	62.1	28.8	1.1	8.0
4	2Pt	350	0.44	84	81	3	54.5	42.6	1.0	1.9
5	2Pt	350	0.88	100	100	0	62.3	22.4	0.9	14.4
6	2Ni	350	0.88	38	32	6	62.1	31.1	1.1	5.7
7	5Ni	350	0.88	78	53	25	60.8	28.4	1.1	9.7
8	1Pt	450	0.88	100	100	0	58.0	40.0	0.7	1.3
9	2Pt	450	0.88	100	100	0	70.0	6.4	0.5	23.1
10	2Ni	450	0.88	48	42	6	68.2	15.5	0.8	15.5
11	5Ni	450	0.88	100	78	22	66.0	17.0	2.0	15.0
12	5Ni	450	1.66	100	80	20	70.0	3.0	2.0	25.0
13	2Ni0.5Pt	450	0.88	71	51	20	60.5	31.3	1.3	6.9

Data collected after 2 h of operation.

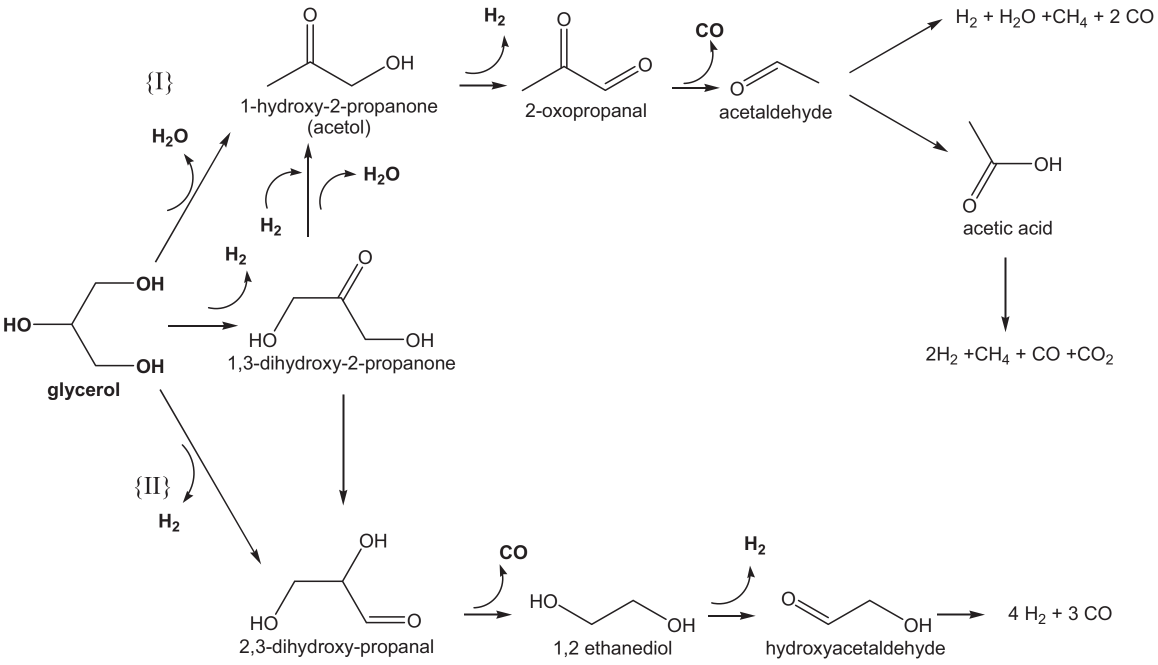

Fig. 3. Schematic reaction pathways for H_2 production by steam reforming of glycerol.

(X_L), total conversion (X_{total}) and the composition of gas products in dry base are represented (H_2, CO, CO_2 and CH_4, in % molar).

First, it is observed that the Ni catalyst can achieve lower total conversion than Pt catalyst in the same experimental conditions. Regarding the distribution of gaseous products, the CO appears as primary product. As the space time increases from 0.44 to 1.6 min, the increase in CO_2 and H_2 production at the expense of CO decrease is noticed (tests no. 1–3). The CH_4 does not present noticeable changes.

At similar total conversion values (see tests no. 1 and 7), the Ni has higher selectivity to CO_2, which evidences the higher contribution of the WGS reaction (Eq. (2)).

To analyze the effect of the metal content, results of tests no. 2 and 4 for 1Pt and 2Pt show similar levels of X_G and X_L, this could indicate that these catalysts maintain the same active phase with increasing metal content. This is in agreement with characterization results, which indicate the same metal dispersion and average particle size for both catalysts.

With respect to temperature, there was an increase in selectivity to H_2 and CO_2 by the contribution of WGS, with increasing temperature from 350 to 450 °C (tests no. 6 and 10). The 5Ni catalyst at 450 °C does not reach total conversion to gas ($X_G = 80\%$), even for the largest space time studied (test no. 12).

The Pt addition to the 2Ni catalyst to generate 2Ni0.5Pt bimetallic catalyst did not improve the catalytic performance (test no. 13). Although the total conversion increased, it was not possible to achieve total conversion to gases. This would indicate that the bimetallic phase affects Pt electronic properties, reducing their ability to C–C cleavage. These results are consistent with those obtained by H_2 chemisorption, where the 2Ni0.5Pt catalyst showed lower H_2 consumption than 2Ni catalyst.

Table 3
Distribution of liquid products for 1Pt, 5Ni and 2Ni0.5Pt.

	1Pt (test no. 1) (%)	2Ni0.5Pt (test no. 13) (%)	5Ni (test no. 7) (%)
Acetaldehyde	8	10	20
2-Oxopropanal	1	5	3
Hydroxy-acetaldehyde	5	4	3
1-Hydroxy-2-propanone	3	3	8
1,2-Ethanediol	68	68	54
1,3-Dihydroxy-2-propanone	10	3	6
2,3-Dihydroxy-propanal	5	7	6

Table 4
Results of activity and carbon content by TPO/TGA of post-reaction samples.

Catalyst	Temperature (°C)	Time on stream (h)	Activity coefficient (a_s)[a]	C deposited (TPO/TGA) (wt%)
1Pt	350	9	0.7	1.8
2Pt	350	40	1	1.3
2Ni	350	7	0.3	8
1Pt	450	40	1	1.2
2Pt	450	40	1	1.4
5Ni	450	20	0.7	14.5
2Ni	450	7	0.5	9.5
2Ni0.5Pt	450	8	0.6	12

[a] Activity coefficient a_s represents the ratio between the glycerol consumption rate at time t (h) and the initial rate.

The analysis of liquid products showed the same reaction intermediates with Ni, Pt and NiPt. The main products were 1,3-dihydroxy-2-propanone, 1-hydroxy-2-propanone, 2-oxopropanal,

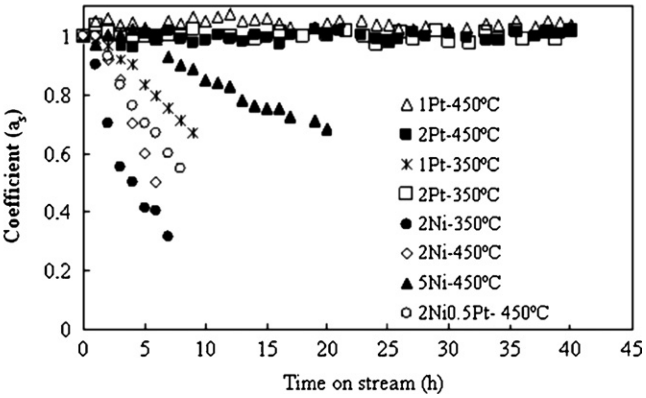

Fig. 4. Results of activity versus time on stream at 350 and 450 °C ($\tau = 0.88$ min).

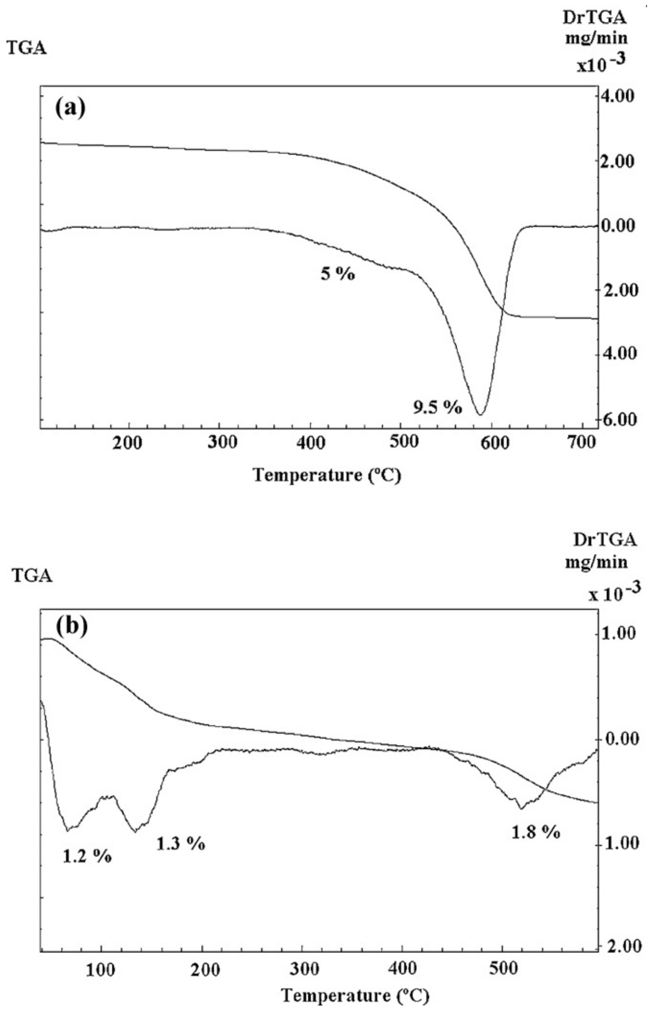

Fig. 5. TPO/TGA analysis. Derivative of weight variation (mg min^{-1}) as a function of temperature. Post-reaction samples: (a) 5Ni and (b) 1Pt.

2,3-dihydroxy-propanal, 1,2-ethanediol, hydroxy-acetaldehyde and acetaldehyde. Table 3 shows the distribution of liquid products of catalysts 1Pt, 5Ni and 2Ni0.5Pt, from tests no. 1, 7 and 13, at similar conversion level. These results would indicate that Ni and NiPt catalysts have the same reaction pathways and they can be explained based on the schematic representation of reaction pathways proposed for Pt/SiO_2 (Fig. 3) [16]. The reaction pathway [I] of this scheme would indicate a first dehydration step leading to acetol. As we have previously shown, the neutral SiO_2 properties do not favor the glycerol dehydration, so this pathway is the least contribution. In the reaction pathway [II] the first step would involve a dehydrogenation leading to formation of 1,3-dihydroxy-2-propanone, or 2,3-dihydroxy-propanal. The conversion of ketone to aldehyde has been reported by FTIR studies [20]. From these early intermediates a sequence of decarbonilation and dehydrogenation reactions occur due to cleavage of C–C bonds. The main contribution of the path [II] is evident from the ratio H_2/CO obtained under lower space times and temperatures. Besides, due to the low CH_4 content in gaseous products, it is reasonable to think that the C–C cleavage predominates over the C–O cleavage.

Fig. 4 and Table 4 show results of activity versus time on stream at 350 and 450 °C determined at $\tau = 0.88$ min. At 450 °C, 2Pt and 1Pt catalysts were stable in the 40 h on stream with an activity coefficient a_s close to 1. 5Ni catalyst showed less stability, with $a_s = 0.7$ at 20 h on stream at 450 °C. Finally, 2Ni0.5Pt and 2Ni had the highest deactivation with $a_s = 0.5$ and 0.6 respectively in 8 h on stream at 450 °C.

The TPO/TGA analyses of post-reaction samples allowed determination of deposited carbon. Pt catalysts showed very low deposited carbon (<2 wt%) compared to Ni catalysts (8–15 wt%).

In the literature, the oxidation temperature has been correlated with the morphology of carbon deposits [21]. Weight losses occurring in the TPO/TGA analysis at temperatures between 250 °C and 480 °C correspond to carbon species highly reactive. The carbon which exhibits a high reactivity to oxidation is located onto or very close to the metal particle. Carbon oxidation temperatures above 480 °C indicate carbon of lower reactivity and the formation of a more ordered structure.

Diagrams of TPO/TGA are shown in Fig. 5(a) and (b) for post-reaction samples 5Ni and 1Pt, respectively. Diagrams show the weight change and the derivatives of weight changes (by oxidation and gasification of carbon) as a function of temperature.

The TPO diagram for 5Ni sample shows that the carbon is eliminated in an oxidizing mixture between 400 °C and 640 °C (Fig. 5(a)). It is noted that the 5% weight loss (at 480 °C) would correspond to the type of amorphous carbon or polymeric species. This type of encapsulant deposit has a strong deactivating character. Moreover the 9.5% weight loss (at 586 °C) could be assigned to the low carbon reactivity and to more ordered structure.

Fig. 5(b) shows the TPO diagram for 1Pt. Weight losses were observed at 80, 140 and 523 °C. From these, only the signal at 523 °C could be assigned to carbon oxidation. Weight losses of 80 °C and 140 °C could correspond to chemisorbed reaction intermediate species, which may be responsible for rapid deactivation of this sample (see Fig. 4), despite very low carbon content of this sample.

4. Conclusions

Different Ni and Pt catalysts supported on SiO_2 have been studied in this article. The study of experimental conditions for the steam reforming reaction of glycerol has demonstrated that using 1Pt and 2Pt catalysts, it is possible to achieve complete conversion to gas at 350 °C with a minimum space time of 1.66 and 0.88 min, respectively. The best results were obtained with 2Pt at 450 °C and $\tau = 0.88$ min, producing a completely gaseous stream of 70% H_2, 6.4% CO, 0.6% CH_4 and 23% CO_2.

The Ni catalysts show significant differences in the selectivity of gas products due to the fact that the Ni catalyzes the WGS reaction in order to remove the CO adsorbed on the surface transforming it into CO_2. The 5Ni catalyst at 450 °C and $\tau = 1.66$ min allowed to obtain only 3% CO.

The Pt addition to the 2Ni catalyst did not improve the catalytic performance, suggesting that the formation of a bimetallic phase would affect the platinum electronic properties. Further studies about the development of the bimetallic catalyst are necessary so as to achieve a system with high selectivity to H_2 and with high stability.

The activity test showed that the 2Pt catalyst allows total conversion to gas, without deactivation during 40 h on stream at 350 °C. It was found that both, the 2Pt catalyst as well as the 1Pt catalyst are stable at 450 °C.

Acknowledgements

We thank the financial support from ANPCyT PICT No. 1962 and CONICET PIP 542.

References

[1] B. Zhang, X. Tang, Y. Li, Y. Xu, W. Shen, International Journal of Hydrogen Energy 32 (13) (2007) 2367–2373.

[2] D.A. Simonetti, E.L. Kunkes, J.A. Dumesic, Journal of Catalysis 247 (2007) 298–306.
[3] S. Adhikari, S. Fernando, S. To, R.M. Bricka, P.H. Steele, A. Haryanto, Energy Fuel 22 (2) (2008) 1220–1226.
[4] A. Iriondo, V.L. Barrio, J.F. Cambra, P.L. Arias, M.B. Guemez, R.M. Navarro, Topics in Catalysis 49 (2008) 46–58.
[5] E.L. Kunkes, D.A. Simonetti, J.A. Dumesic, W.D. Pyrz, L.E. Murillo, J.G. Chen, D.J. Buttrey, Journal of Catalysis 260 (2008) 164–177.
[6] E.L. Kunkes, R.R. Soares, D.A. Simonetti, J.A. Dumesic, Applied Catalysis B: Environmental 90 (2009) 693–698.
[7] V. Chiodo, S. Freni, A. Galvagno, N. Mondello, F. Frusteri, Applied Catalysis A: General 381 (2010) 1–7.
[8] K. Lehnert, P. Claus, Catalysis Communications 9 (2008) 2543–2546.
[9] N. Luo, X. Fu, F. Cao, T. Xiao, P.P. Edwards, Fuel 87 (2008) 3483–3489.
[10] D.L. King, L. Zhang, G. Xia, A.M. Karim, D.J. Heldebrant, X. Wang, T. Peterson, Y. Wang, Applied Catalysis B: Environmental 99 (2010) 206–213.
[11] A. Wawrzetz, B. Peng, A. Hrabar, A. Jentys, A.A. Lemonidou, J.A. Lercher, Journal of Catalysis 269 (2010) 411–420.
[12] T. Valliyappan, D. Ferdous, N.N. Bakhsi, A.K. Dalai, Topics in Catalysis 49 (2008) 59–67.
[13] P.J. Dauenhauer, J.R. Salge, L.D. Schmidt, Journal of Catalysis 244 (2006) 238–247.
[14] S.M. Swami, M.A. Abraham, Energy Fuel 20 (2006) 2616–2622.
[15] I.N. Buffoni, F. Pompeo, G.F. Santori, N.N. Nichio, Catalysis Communications 10 (2009) 1656–1660.
[16] F. Pompeo, G.F. Santori, N.N. Nichio, International Journal of Hydrogen Energy 35 (2010) 8912–8920.
[17] E. Merlen, P. Beccat, J.C. Bertolini, F. Delichere, N. Zanier, B. Didillon, Journal of Catalysis 159 (1996) 178.
[18] O. Clause, L. Bonneviot, M. Che, Journal of Catalysis 138 (1992) 195.
[19] B. Pawelec, S. Damyanova, K. Arishtirova, J.L.G. Fierro, L. Petrov, Applied Catalysis A: General 323 (2007) 188–201.
[20] V.A. Yaylayan, S. Harty-Majors, A.A. Ismail, Carbohydrate Research 318 (1999) 20–25.
[21] D. Duprez, M. Demicheli, P. Marecot, J. Barbier, O. Ferretti, E. Ponzi, Studies in Surface Science and Catalysis 68 (1991) 195.