Effect of Active Metal Supported on SiO₂ for Selective Hydrogen Production from the Glycerol Steam Reforming Reaction

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The performance of nickel, cobalt, and copper supported on silica as catalysts was evaluated for the glycerol steam reforming (GSR) reaction. The samples were characterized by nitrogen-porosimetry according to Brunauer-Emmett-Teller (BET) method, X-ray diffraction (XRD), and inductively coupled plasma atomic emission spectroscopy (ICP-AES), while the deposited carbon on the catalytic surface was measured with a CHN-analyzer. Catalysts were studied in order to investigate the effect of the reaction temperature on (i) glycerol total conversion, (ii) glycerol conversion to gaseous products, (iii) hydrogen selectivity and yield, (iv) selectivity of gaseous products, and (v) selectivity of liquid products. The results showed that the Ni based on silica (Ni/Si) catalyst was more active and produced less liquid effluents than the catalysts that used an active metal such as Co or Cu. Moreover, the H₂ yield from the Ni/Si catalyst was very close to the theoretical maximum predicted by thermodynamics, and the CO₂ production was favoured in comparison to CO production, which is important for use in fuel cells.

Keywords: Hydrogen; Glycerol; Steam Reforming; SiO₂ supported catalysts; Biodiesel

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INTRODUCTION

Arguably, fossil fuels have helped us build our current civilization, created our wealth, and enriched the lives of billions. However, they also create rising costs to our security, economy, health, and environment that are starting to erode if not outweigh their benefits. Among the various renewable energy systems (RES) that have been developed, the use of biomass as a potential energy provider has gained considerable attention, especially in the field of biofuels, as the only realistic alternative to petro-oil (Yeon *et al.* 2013; Panepinto *et al.* 2014).

Biodiesel is mainly produced from the transesterification reaction between vegetable oils or animal fats (mainly, sunflower, rapeseed oils, palm oil, canola oil, cotton seed, soybean, *Jatropha curcas*, algae, waste frying oils, non-edible oils, *etc.*) and methanol (although ethanol is also used to a lesser extent) in the presence of an acidic or alkaline catalyst to form the fatty acid methyl esters (FAME) or fatty acid ethyl esters (*i.e.*, biodiesel) as shown in Eq. 1 (Atadashi *et al.* 2013; Atapoour and Kariminia 2013; Marx and Venter 2014).

$$C_{3}H_{5}(OOC)_{3}(R_{n})_{3} + 3R'OH \in 3R_{n}COOR + C_{3}H_{5}(OH)_{3}$$

$$(1)$$

$$Esters Glycerol$$

Over the past decade, biodiesel has moved from being a niche energy source in the European transport sector to being a significant source of road transport fuel, with the EU 27 experiencing an increase in the use of biodiesel of over 3000% between 2000 and 2012 (USEIA 2015). This number is assured to increase further due to the policies that are been pursued by the European Union (EU) (Murphy *et al.* 2014; Yunus Khan *et al.* 2014).

The main byproduct of the biodiesel industry is glycerol, as every 100 g of oil undergoing transesterification produces 10 g of glycerol as byproduct. The glycerol obtained is crude, as it contains non-reacted and partially-reacted fats, free fatty acids, methanol, esters, and salts, and thus, it cannot be used as a raw material in the pharmaceutical and cosmetic industries (Khanna *et al.* 2014). A viable solution could be the reconstruction of biodiesel plants into novel biorefineries through the integration of glycerol-based bioconversions in existing lines for the production of various chemicals (Kachrimanidoy *et al.* 2013) or the production of syngas and hydrogen (Escribà *et al.* 2011). Moreover, it is important to note that the excess of crude glycerol produced (Fig. 1) by the biodiesel industry (exceeding 2 million metric tons in 2012), is a serious waste management issue (Almeida *et al.* 2012) that needs to be addressed.



Fig. 1. World and EU-28 glycerol production in millions of tones per year from 2007 to 2012 (calculations based on an average biodiesel density of 0.86 g/cm³) (USEIA 2015)

However, glycerol could potentially be used to produce hydrogen, a clean energy source with numerous uses whose demand is expected to greatly increase in the future, mainly due to technological advancements in the fuel cell industry (Amoretti 2011; Pudukudy *et al.* 2015). Hydrogen can be produced from glycerol by catalytic steam reforming (SR) (Adhikari *et al.* 2007; Buffoni *et al.* 2009; Iriondo *et al.* 2009; Cheng *et al.* 2011; Wang *et al.* 2013), oxidative steam reforming (Alvarado and Gracia 2012), autothermal reforming (ATR) (Dauenhauer *et al.* 2006; Wang *et al.* 2009), aqueous phase

reforming (APR) (Cortright *et al.* 2002; Manfro *et al.* 2011; Menezes *et al.* 2011; Tuza *et al.* 2013), and supercritical water (SCW) reforming reactions (Byrd *et al.* 2008; Gutiérrez Ortiz *et al.* 2013; Pairojpiriyakul *et al.* 2013). However, steam reforming has attracted the most attention, partially due to the fact that the process is widely used in industry, and it would require only minor alterations in existing systems if the feedstock was changed from natural gas or naphtha to glycerol (Silva *et al.* 2015).

Based on this background, a comparative study of the catalytic performances of nickel (Ni), cobalt (Co), and copper (Cu) supported on silica catalysts, for the glycerol steam reforming reaction, is reported in this study. Catalysts were synthesized applying the incipient wetness impregnation method at a constant metal loading (5 wt.%). The synthesized samples were characterized by N_2 porosimetry (Brunauer-Emmett-Teller (BET) method) at their calcinated form and by X-ray diffraction (XRD) analysis at their calcinated forms. The chemical composition of the catalysts was determined by inductively coupled plasma atomic emission spectroscopy (ICP-AES), while the deposited carbon on the catalytic surface during the reaction was measured by a carbon-hydrogen-nitrogen (CHN) analyzer. Catalyst performance for the glycerol steam reforming was studied in order to investigate the effect of the reaction temperature on (i) glycerol total conversion, (ii) glycerol conversion to gaseous products, (iii) hydrogen selectivity and yield, (iv) selectivity of gaseous products, and (v) selectivity of liquid products.

EXPERIMENTAL

Preparation and Characterization of Catalysts

The silica support, which was obtained from Engelhard Corp. (NJ, USA; SDS code: SI-1624E), was sieved to 350 to 500 μ m particle size, before being calcined at 800 °C for 4 h. The catalysts were prepared *via* the incipient wetness impregnation method (Goula *et al.* 2015) by impregnating the SiO₂ with Ni(NO₃)₂·6H₂O, Co(NO₃)₂·6H₂O, and Cu(NO₃)₂·6H₂O aqueous solutions having the appropriate concentrations, in order to obtain 5 wt.% Ni, Co, and Cu, respectively in the final catalysts. These catalysts were labelled Ni/Si, Co/Si, and Cu/Si. The total volume of the impregnated solutions was equal to the total pore volume of the silica used. The impregnated samples were dried overnight and calcined at 800 °C for 5 h. All solutions used for catalyst preparation employed distilled and deionised pure water generated by a NANOpure Diamond UV unit (Barnstead International, Dubuque, USA).

Surface areas (S_{BET}) of the catalytic samples were determined by the N₂ adsorption-desorption isotherms at -196 °C using the Nova 2200e (Quantachrome, Boynton Beach, USA) flow apparatus, according to the BET method at the relative pressure range of 0.05 to 0.30. The total pore volume calculation was based on nitrogen volume at the highest relative pressure, whereas the average pore size diameter was determined by the Barrett-Joyner-Halenda (BJH) method. Prior to the measurements, the samples were degassed at 350 °C for 5 h under vacuum.

The total metal loading (wt.%) in the catalysts was determined by ICP-AES on a Perkin-Elmer Optima 4300DV apparatus (Waltham, USA). The wavelengths selected were \approx 342, 227, and 232 nm. The selected conditions for the measurement were as

follows: plasma flow, 15 L/min; auxiliary flow, 0.2 L/min; nebulize flow, 0.6 L/min; RF power, 1300 watt; plasma view, radial view; and sample flow rate, 2 mL/min.

The catalyst crystalline structure was determined by X-ray diffraction (XRD) using a ThermoAl diffractometer (Waltham, USA) at 40 kV and 30 mA with Cu K_a radiation ($\lambda = 0.154178$ nm). The diffractograms were recorded in the $2\theta = 2$ to 70° range at a scanning rate of 0.04 over 1.2 min. The diffraction pattern was identified by comparison with those of known structures in the Joint Committee of Powder Diffraction Standards (JCPDS) database (Charisiou *et al.* 2016). XRD was used for both fresh and reduced samples.

The percentile concentration of carbon in the used catalysts was measured by quantitative infrared spectroscopy performed with a Leco CHN-200 analyser (St. Joseph, USA) using 0.1 g of each sample.

Catalytic Performance

The glycerol steam reforming reaction was carried out at atmospheric pressure, in a continuous flow, fixed-bed, single pass, tubular stainless steel reactor, with an inner diameter of 14 mm, at temperature ranging from 400 to 750 °C (Fig. 2). The experimental set-up allowed the feeding of both liquid and gaseous streams, having two vaporizers, to vaporize glycerol at 350 °C, and a pre-heater before the reactor and a condenser after it to obtain the liquid products. The vaporizers, pre-heater, and the reactor were placed into electrical ovens and regulated with programmed-temperature controllers.



Fig. 2. Experimental setup for testing catalyst activity during glycerol steam reforming

The liquid stream consisted of $C_3H_8O_3$ (20 wt.%) and H_2O (total liquid flow rate of 0.12 mL/min). The glycerol used had 99.5% purity and was obtained from Sigma Aldrich (St. Louis, USA). The glycerol/water mixture was fed with an HPLC Series I pump (Scientific Systems Inc, Woburn, USA) and was first vaporized at 350 °C before it was mixed with He (He flow rate of 38 mL/min). The reactor's outlet gases were passed through a cold trap for liquid products capture.

Prior to catalytic testing, 200 mg of undiluted catalyst (the catalyst bed was supported by quartz wool) was reduced *in situ* under a flow of 100 v/v% hydrogen (100

mL min⁻¹) at 800 °C for 1 h. The catalyst was then purged with helium for 45 min, the temperature was lowered to 750 °C, and the reaction feed was introduced into the catalyst bed. In order to ensure operation at steady state conditions, the catalyst was left for approximately 50 min at each step. Liquid products were obtained at the end of this 50 min period.

The gaseous products were analyzed on-line by a gas chromatographer (Agilent 7890A, Santa Clara, USA), with two columns in parallel, HP-Plot-Q (19095-Q04, 30 m length, 0.530 mm I.D.) and HP-Molesieve (19095P-MSO, 30 m length, 0.530 mm I.D.), equipped with a thermal conductivity detector (TCD) and a flame ionization detector (FID). Liquid products were analyzed *via* a combination of gas chromatography (Agilent 7890A, with a 5MS column, equipped with an FID detector) and mass spectroscopy (Agilent 5975C).

Catalytic performance was reported in terms of H₂ yield, H₂, CO, CH₄, and CO₂ selectivity, glycerol conversion into gaseous products, and total glycerol conversion. Moreover, the performance of the catalysts in the liquid phase was reported in terms of acetol (C₃H₆O₂), acetone [(CH₃)₂CO], allyl alcohol (CH₂=CHCH₂OH), acetaldehyde (C₂H₄O), and acetic acid (C₂H₄O) selectivity. Performance parameters were calculated based on the following equations:

% glycerol conversion_(global conversion) =
$$\left(\frac{Glycerol_{in} - Glycerol_{out}}{Glycerol_{in}}\right) \times 100$$
 (2)

% glycerol conversion_(gaseous products) =
$$\left(\frac{C \text{ atoms in the gas products}}{\text{total } C \text{ atoms in the feedstock}}\right) \times 100$$
 (3)

$$H_2 \text{ yield} = \frac{H_2 \text{ moles produced}}{\text{moles of glycerol in the feedstock}}$$
(4)

$$\% H_2 \ selectivity = \left(\frac{H_2 \ moles \ produced}{C \ atoms \ produced \ in \ the \ gas \ phase}\right) \times \left(\frac{1}{RR}\right) \times 100$$
(5)

where RR is the reforming ratio (7/3), defined as the ratio of moles of H₂ to CO₂ formed.

% selectivity of
$$i = \left(\frac{C \text{ atoms in species } i}{C \text{ atoms produced in the gas phase}}\right) \times 100$$
 (6)

where, species i refers to CO, CO₂, and CH₄.

% selectivity of
$$i' = \left(\frac{C \text{ atoms in species } i'}{C \text{ atoms produced in the liquid phase}}\right) \times 100$$
 (7)

where species *i*' refers to acetol, acetone, allyl alcohol, acetaldehyde, and acetic acid.

RESULTS AND DISCUSSION

Characterization of Catalyst

The physicochemical properties of all samples are presented in Table 1. The specific surface area (SSA, *i.e.*, S_{BET}) and the pore volume (*V*p) for all catalysts was lower than that of the supporting material. The lower surface area can be attributed to the fact that the internal surface area of the supporting material is probably progressively covered by Ni, Co, and Cu, species forming a layer (Bereketidou and Goula 2012; Charisiou *et al.* 2016). Nonetheless, all three catalytic samples had comparable S_{BET} and *V*p values. Moreover, the ICP results indicated that the desired metal loading levels were achieved for all samples.

Sample	S _{BET} (m²/g)	V _p (mL/g)	Metal Loading ICP (wt.%)	Carbon Deposition (% on Used Samples)		
SiO ₂	108.27	0.86	-			
Ni/Si	84.09	0.69	4.86	23.62		
Co/Si	87.01	0.74	4.73	9.97		
Cu/Si	71.92	0.64	4.85	12.65		

Table 1. Physicochemical Properties of the Calcined and Used Samples

Figure 3 depicts the XRD patterns of the Ni/Si, Co/Si, and Cu/Si catalysts after calcination and after reduction. Characteristic peaks at $2\theta = 21.9^{\circ}$, corresponding to SiO₂ (cristobalite) and $2\theta = 26.5^{\circ}$ corresponding to SiO₂ (quartz) were observed for all samples. The nickel oxide (NiO) structure was detected at $2\theta = 37.2^{\circ}$ and 43.2° on the calcined sample (which correspond to NiO(111) and (012), respectively; these peaks are well defined due to the decomposition of nickel nitrate in air at the high calcination temperature used in this study.

On the reduced Ni/Si sample, two small peaks due to the presence of metallic nickel (Ni⁰) at $2\theta = 44.3^{\circ}$ and 51.7° (Fig. 3a) were observed. From the diffractograms of the Co/Si catalyst (Fig. 3b), characteristic peaks at $2\theta = 31.2^{\circ}$, 36.7° , 44.6° , 55.5° , 59.1° , and 64.9° indicated the presence of cobalt oxide (Co₃O₄) on the calcined sample, while metallic cobalt (Co⁰) was detected at $2\theta = 44.05^{\circ}$ and 51.4° on the reduced sample. In regards to the diffractograms of the Cu/Si catalyst (Fig. 3c), copper oxide (CuO) was detected at $2\theta = 35.5^{\circ}$, 38.6° , 48.5° , and 62.5° on the calcined sample; the fact that these peaks are well defined in the XRD pattern may be an indication that CuO is not highly dispersed on to the support or that CuO crystals have relatively large sizes. For the reduced sample, metallic Cu (Cu⁰) at $2\theta = 43.24^{\circ}$ and 50.36° was observed.

Catalytic Activity and Selectivity

Thermodynamic studies predict that high temperatures, low pressures, and high H₂O/C ratio favour hydrogen production. Researchers have suggested that the ideal condition to obtain hydrogen is at reaction temperatures between 627 and 700 °C, with a molar ratio of water to glycerol higher than 9. Under these conditions, minimum methane production is predicted, and carbon formation is thermodynamically inhibited (Adhikari *et al.* 2007; Wang *et al.* 2008; Iriondo *et al.* 2009; Franchini *et al.* 2014; Freitas and

Guirardello 2014; Sad *et al.* 2015). Thus, in this work, reaction tests were carried out in the range 400 to 750 °C, at atmospheric pressure and a water-glycerol molar ratio of 20:1.



Fig. 3. XRD patterns of calcined and reduced (a) Ni/Si, (b) Co/Si, and (c) Cu/Si catalysts

Glycerol total conversion and glycerol conversion into gaseous products are presented in Fig. 4. All three catalysts showed improvements with increased temperatures, which is a consequence of the endothermic nature of the overall steam reforming reaction. However, the Ni/Si catalyst exhibited noticeable higher conversions into gaseous products.

As can be observed from Fig. 4, the sequence of catalytic performance is Ni/Si > Co/Si > Cu/Si. Glycerol total conversion was essentially flat for all the catalysts, with the Cu/Si sample performing poorer for the low temperature range. It should be noted that this high glycerol total conversion has been observed by all researchers that have investigated this reaction (Cheng *et al.* 2011; Ebshish *et al.* 2012).



Fig. 4. Total glycerol conversion and glycerol conversion into gaseous products for the Ni/Si, Cu/Si, and Co/Si catalysts

GC analysis revealed that the gaseous products were H₂, CO₂, CO, and CH₄, which agreed with previous work showing that these are the major gaseous products of glycerol steam reforming at 400 °C (Hirai *et al.* 2005; Zhang *et al.* 2007; Dou *et al.* 2014; Siew *et al.* 2014; Gallegos-Suárez *et al.* 2015). Hydrogen yield and selectivity (%) are presented in Fig. 5. The hydrogen selectivity increased with increasing temperatures for all catalysts; however, their behaviour was not similar. The selectivity for the Cu/Si sample began at low values ($\approx 25\%$) at 400 °C and increased sharply up to 500 °C; from then on it almost reached a plateau. In contrast, for both Ni/Si and Co/Si samples, the hydrogen selectivity had high initial values ($\approx 70\%$ and $\approx 50\%$, respectively), but the increase was very gradual, also almost terminating at 500 °C. The sequence of catalytic performance in terms of H₂ yield (moles_{H2}/ moles_{glycerol}) was again Ni/Si > Co/Si > Cu/Si (Fig. 5). Notably, although the Co/Si sample exhibited higher hydrogen yield than the Cu/Si sample between 400 to 600 °C, above this temperature the two catalysts displayed similar selectivity. Most importantly, the H₂ yield of the Ni/Si catalyst (5.2 mol) was close to the theoretical maximum value (6.0 mol) predicted by thermodynamics.



Fig. 5. Hydrogen yield and selectivity for the Ni/Si, Cu/Si, and Co/Si catalysts

In Table 2 the influence of the reaction temperature, ranging from 400 to 750 °C, on the selectivity values of the gaseous and liquid products is presented. It can be noted that for the Ni/Si catalyst the CH₄ and CO₂ production followed a volcano-type curve (reaching almost the same value at 700 °C) with its peak between 450 and 500 °C, while a reverse volcano can be evidenced for CO. For the Co/Si catalyst the same trend can also be observed to a lesser extent for the CO₂ and CO, with the only difference being that these values were lower (higher) at 700 °C than at 400 °C, while CH₄ production seems to have increased with temperature. As for the Cu/Si sample there was a clear decreasing trend for CO₂ and CH₄ production, while the opposite can be observed for the CO.

Acetol, acetone, allyl alcohol, acetaldehyde, and acetic acid are the main liquid products that could be detected for the reaction temperature ranging between 400 and 600 °C for the Ni/Si, 400 to 700 °C for the Co/Si, and 400 to 750 °C for the Cu/Si sample. It should be also mentioned that acetol was the main liquid product for all samples for T < 600 °C. Above this temperature, allyl alcohol was the main product for the Ni/Si catalyst, and acetone and acetaldehyde for the Co/Si and Cu/Si, respectively. Acetol production seems to have been maximized for T ranging from 450 to 550 °C for all catalysts, while it reached zero at T value equal to 650 and 750 for the Ni/Si, Co/Si and Cu/Si samples, respectively. On the other side, acetone production went through its minimum values for the same temperature range (450 to 550 °C) and it exhibited an increasing trend for higher T, reaching its maxima at 600, 700, and 750 °C for the Ni/Si, Co/Si, and Cu/Si samples, respectively. Production of allyl alcohol was constant for all samples at T values lower than 550 °C, tending to increase for the Ni/Si (T=600 °C) and Cu/Si (T=600 to 700 °C) and to decrease for Co/Si (T=600 °C). Acetaldehyde production followed the same trend with temperature, with the only difference that its values increased for all samples for T higher than 550 °C, reaching zero at 650 °C for the Ni/Si and at 700 °C for the Co/Si (in the case of Cu/Si its value remains high even at 750 °C). Finally, acetic acid selectivity increased with temperature for all samples, reaching its zero value at 650, 600, and 700 °C for the Ni/Si, Co/Si, and Cu/Si, respectively.

A more in depth analysis of the experimental results presented herein, requires discussing the reactions associated with the hydrogen production during the glycerol steam reforming, mainly:

$$C_{3}H_{8}O_{3}(g) + 3H_{2}O(g) \rightarrow 3CO_{2}(g) + 7H_{2}(g)$$
 (8)

$$C_3H_8O_3(g) \to 3CO(g) + 4H_2(g) \tag{9}$$

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g) \tag{10}$$

Equation 8 represents the overall steam reforming reaction, an endothermic transformation that could be considered as the contribution of the other two reactions, namely glycerol decomposition (Eq. 9) and water gas shift (WGS, Eq. 10).

It should be mentioned that the overall reaction pathway is thought to be quite complex, as many other reactions can also take place, in particular CO and CO_2 hydrogenation leading to methane formation. Some other side reactions can also take place, such as dehydration, dehydrogenation, cyclization, and polymerization, that lead to carbon deposition (Cheng *et al.* 2010; Chiodo *et al.* 2010). In the generally accepted mechanism of metal catalyzed glycerol steam reforming, the rate determining step is C–C

cleavage, which leads to adsorbed CO. Carbon monoxide must be removed from the catalyst surface by the water–gas shift reaction, because high surface coverage by CO decreases the catalytic activity (Nichele *et al.* 2012).

In recently published works (Papageridis *et al.* 2016; Goula *et al.* 2016a,b), the authors also have reported that the Ni/Al catalyst reveals an improved ability to convert glycerol into gaseous products, in comparison with the Co/Al and Cu/Al, due to its superior capacity to promote the necessary C–C rupture. It has also revealed a superior ability for H₂ production with the CH₄ formation almost inhibited for temperatures above 600 °C, while the CO production at the high temperature range can be attributed to the reverse water gas shift (RWGS) reaction. As for the liquid products, the production of acetaldehyde, acetone, allyl alcohol, acetic acid, acrolein and acetol was observed for all catalysts at temperatures below 650 °C, while their varying distribution confirms the complexity of the process, with reactions as dehydration, dehydrogenation, and hydrogenolysis taking place.

Pompeo *et al* (2011) prepared Pt and Ni catalysts supported on SiO₂ in order to test them in the reaction of glycerol's steam reforming at temperatures ranging from 350 °C to 450 °C. Based on the identification of liquid products or reaction intermediates, the authors reported 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 H₂ and CO. Furthermore, the catalytic performance concerning conversion, selectivity and stability were evaluated with the Pt catalysts being more active and stable, while Ni catalysts showed differences in the selectivity to gaseous products due to the increased contribution of the WGS reaction.

Sad *et al.* (2015) reported that Pt supported over an inert solid (Pt/SiO₂ sample) improves the steam reforming reaction by catalyzing the C-C, C-H, and O-H bonds cleavage and preventing C-O scissions that conduct to undesirable liquid products and also the hydrogenation of CO or CO₂ that produce light alkanes. It is important to remark that the SiO₂ showed neither basic nor acid properties and was not active for steam reforming reaction. Thus, the present results are in good agreement with the information available in the literature suggesting that the selection of a non-acidic support is appropriate to syngas and/or hydrogen production *via* steam reforming reaction of several oxygenates compounds derived from biomass (Soares *et al.* 2006; Ni *et al.* 2007; Ciambelli *et al.* 2010).

Rosseti *et al.* (2014) investigated ethanol steam reforming in the low temperature range, focusing not only on H₂ productivity, but also on catalyst stability. Different supports (SiO₂ and ZrO₂), active phases (Ni, Co, Cu) and reaction temperature (300 to 500 °C) have been employed. It has been confirmed that Ni is the best performing active phase to promote ethanol decomposition and reforming already at low reaction temperature. Different reaction paths have been observed (*i.e.* different byproducts) depending on the active phase, but also on the support. In particular, Co and Cu were predominantly active for ethanol dehydrogenation. Their reforming activity for the conversion of acetaldehyde was very poor, whereas conversion with Co took place at 500 °C. However, poor activity was achieved when temperatures decreased. By contrast, both the Ni-based catalysts were active at very low reaction temperature (300 °C). Stability toward coking seems to be a major problem, even if the support nature plays a key role

from this point of view. SiO_2 showed itself to be an interesting support for Ni catalysts due to no Lewis acidity and sufficiently strong metal–support interaction.

Gas Phase Product Selectivity											
Compounds Reaction temperature (°C)											
Compounds	400	450	500	550	600	650	700	750			
Ni/Si											
Methane	6.98	9.32	8.84	6.59	5.96	5.64	7.41	4.70			
Carbon dioxide	52.26	60.24	61.33	57.92	50.26	46.41	54.79	60.67			
Carbon monoxide	40.77	30.44	29.84	35.49	43.77	47.95	37.81	34.63			
Co/Si											
Methane	0.00	4.34	3.93	5.53	6.48	9.38	12.05	7.64			
Carbon dioxide	59.41	62.25	60.71	54.65	29.69	25.34	34.76	34.06			
Carbon monoxide	40.59	33.42	35.36	39.81	63.83	65.28	53.18	58.29			
			С	u/Si							
Methane	0.00	9.14	5.19	3.71	3.83	4.68	5.11	3.75			
Carbon dioxide	58.57	50.17	47.94	44.12	41.77	41.63	43.76	44.08			
Carbon monoxide	41.43	40.69	46.88	52.17	54.40	53.70	51.14	52.16			
Liquid Product Selectivity											
	_	_	<u> </u>	li/Si	-						
Acetol	44.83	46.08	44.73	47.01	8.77	0.00	0.00	0.00			
Acetone	13.11	11.67	11.42	12.18	16.35	0.00	0.00	0.00			
Allyl alcohol	18.13	18.98	19.80	15.67	31.68	0.00	0.00	0.00			
Acetaldehyde	12.53	11.88	12.21	12.48	20.81	0.00	0.00	0.00			
Acetic acid	11.40	11.38	11.84	12.66	22.40	0.00	0.00	0.00			
	1	1	C	o/Si		r	1				
Acetol	34.95	37.16	42.50	26.67	15.78	0.00	0.00	0.00			
Acetone	16.63	14.06	14.69	19.08	39.73	56.18	100	0.00			
Allyl alcohol	19.84	19.36	20.58	20.74	13.98	0.00	0.00	0.00			
Acetaldehyde	20.03	21.12	12.25	17.31	30.51	43.82	0.00	0.00			
Acetic acid	8.56	8.31	9.98	16.20	0.00	0.00	0.00	0.00			
	1	1	C	u/Si		r	1				
Acetol	34.25	39.64	39.53	39.38	30.30	2.68	3.42	0.00			
Acetone	21.31	10.27	12.10	13.35	14.78	22.67	26.44	55.17			
Allyl alcohol	24.50	27.97	22.31	19.97	23.94	33.05	24.29	0.00			
Acetaldehyde	12.53	13.71	16.09	17.04	17.77	24.11	25.81	44.83			
Acetic acid	7.41	8.42	9.97	10.26	13.20	17.49	20.04	0.00			

Table 2. Selectivity of Gaseous and Liquid Products (9
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Regarding carbon deposition, it has been reported that both Ni and Co catalysts favored the formation of CNTs (Bethune *et al.* 1993; Natha *et al.* 2000; Kurasawa *et al.* 2002). It is also known from the abundant literature on CH₄ reforming that smaller Ni particles are less prone to coking than larger ones. The reason for such behavior should be attributed to the mechanism of coke formation over Ni (Christensen *et al.* 2006; Gonzalez-Dela Cruz *et al.* 2008; Centi and Perathoner 2009). As a matter of fact, the growth of carbon nanofibers in such cases involves methane adsorption on the surface and its conversion into adsorbed carbon (Chen *et al.* 2005). Then, carbon segregates into the layers near the surface by diffusion through Ni and precipitation on the rear side of

the Ni crystal. Smaller Ni crystal size results in a larger saturation concentration, leading to a lower driving force for carbon diffusion and hence a lower coking rate.

Finally, Ni-based catalysts supported on TiO₂, ZrO₂, and SiO₂ (SBA-15 and amorphous dense nanoparticles), were employed in the steam reforming of glycerol (Rosseti et al. 2013). It was confirmed that the stronger metal-support interaction, the more stable the metallic Ni clusters, which in turn lead to a higher catalytic activity and stability. Surface acidity was also taken into account, in which the nature of the acid sites was differentiated (silanols, titanols, or Lewis acid sites). Characterization of the spent catalysts was also interpreted with the deactivation process, while the formation of multiwalled nanotubes was observed for every sample, though it was only in some cases that this led to severe deactivation. The attribution of most carbonaceous species to MWCNTs has been confirmed by FE-SEM analysis, which clearly shows the morphology of carbon deposits over spent samples. Carbon nanotubes were evident on every used catalyst, with slightly different morphologies and distributions that depended on the support and, secondarily, on the preparation method. The diameter of nanotubes ranged between 35 and 50 nm for most samples. Furthermore, the surface of NiSiF was more fully and uniformly covered by the carbonaceous residue than other samples and the diameter was the lowest (35 to 40 nm).

CONCLUSIONS

- 1. Glycerol valorization into hydrogen is one of the prospective ways to alleviate the dependence on fossil fuels.
- 2. All catalysts tested herein exhibited very high total glycerol conversions. Ni/Si showed the highest conversion into gaseous products, while over 600 °C this catalyst produced no liquid effluents. Moreover, the H₂ yield of the Ni/Si catalyst was very close to the theoretical maximum predicted by thermodynamics, and CO₂ production is favoured in comparison to CO production, which is important for use in fuel cells.

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