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Steam reforming of glycerol: Hydrogen production optimization

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ABSTRACT

The glycerol steam reforming reaction was studied using Pt-based catalysts in order to selectively produce hydrogen. The global steam reforming reaction is the combination of two consecutive steps: i) glycerol decomposition and ii) water gas shift reaction (WGS).

Pt supported over solids with markedly different physicochemical properties (SiO_2, MgO, Al_2O_3 and TiO_2) were prepared and tested in steam reforming reaction of glycerol (10% wt. aqueous solution) at 573–623 K. Glycerol to gas products conversion of 100% and hydrogen yield of 78.8% were obtained by using Pt over an inert support (Pt/SiO_2 prepared from chlorine-free solution). Acidic supports favored undesirable reactions conducting to liquid products and coke precursors. Furthermore, WGS reaction was studied at reaction conditions compatible with steam reforming over Pt/SiO_2, Pt/TiO_2 and two catalysts prepared for that purpose: Pt/CeO_2 and Pt/ZrO_2. Pt/TiO_2 showed the highest CO conversion at 623 K. In order to maximize H_2 formation, a double-bed catalytic system (0.5% wt. Pt/SiO_2 + 0.5% wt. Pt/TiO_2) was used achieving a 100% hydrogen yield without deactivation on stream.

Introduction

The depletion of worldwide oil supplies together with current awareness of the need to find alternative forms of energy from renewable resources are the main motivation for the study and development of new technologies for the production of both liquid and gaseous fuels. Carbon dioxide is the main greenhouse gas associated with global warning; it is produced in all combustion processes involving fossil fuels as well as in other industrial processes such as cement production and sweetening of natural gas [1]. One-fifth of global carbon dioxide emissions are created by the transport sector, which accounts for about 60% of global oil consumption [2]. Therefore, alternate transportation fuels, such as bioethanol, biodiesel, and hydrogen, will play an important role in the world's future [3,4]. Concretely, hydrogen has a high energy yield of 122 kJ/g, which is 2.75 times greater than hydrocarbon fuels [5] and is a clean fuel with no CO_2 emissions that can easily be used in fuel cells for generation of electricity. Hydrogen can be produce by using different technologies from a wide variety of primary energy sources [6]. However, approximately 90% of the hydrogen produced nowadays comes from nonrenewable carbonaceous raw material [7]. Currently, much research has

been focused on sustainable and environmental friendly energy from biomass to replace conventional fossil fuels; besides biomass and biomass-derived fuels can be used to sustainably produce hydrogen [8].

Glycerol is obtained on a large amounts in South American countries as a byproduct of biodiesel production; also can be obtained from fermentation of sugars such as glucose either directly or as sub-product of lignocellulose into ethanol conversion [9]. Although glycerol is a very versatile product and it can be used in food, beverages, pharmaceuticals and to produce a variety of chemicals [10,11], a large excess is sold at low prices and therefore, is interesting to find viable processes to obtain products with higher added value and/or fuels from this molecule. Fig. 1 shows several possible reactions from glycerol to get more valuable products such as dehydration, oxidation, etherification, esterification, cracking, hydrogenolysis and C–C and C–O cleavages leading to H_2, CO and CO_2 or alkanes/alkenes respectively. The routes showed in Fig. 1 are not exhaustive but accounts for the numerous ways to produced chemicals or fuels from an abundant and inexpensive renewable source such as glycerol. As it is remarked in Fig. 1, we will focus in the present paper on selective H_2 production from this polyol via steam reforming reaction.

The overall steam reforming reaction is an endothermic reaction ($\Delta H^0 = 123$ kJ/mol, Reaction (1)) and it is the result of combination of glycerol decomposition (Reaction (2), $\Delta H^0 = 245$ kJ/mol) and Water Gas Shift (WGS, Reaction (3)) [12].

$$C_3O_3H_8 + 3H_2O \leftrightarrow 3CO_2 + 7H_2 \quad \text{(Reaction 1)}$$

$$C_3O_3H_8 \leftrightarrow 3CO + 4H_2 \quad \text{(Reaction 2)}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \text{(Reaction 3)}$$
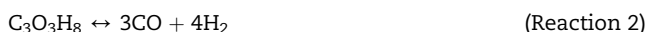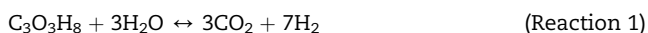
The CO/H_2 ratio formed by glycerol steam reforming depends on the reaction conditions and the catalyst employed. The CO obtained from glycerol decomposition may further react in presence of water to form CO_2 by the exothermic ($\Delta H^0 = -41$ kJ/mol) WGS reaction. Additionally, methane formation may proceed from CO or CO_2 and H_2 by two also exothermic reactions (Reactions (4) and (5), $\Delta H^0 = -206$ kJ/mol and $\Delta H^0 = -165$ kJ/mol respectively) [12].

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

$$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O \quad \text{(Reaction 5)}$$

In order to favor H_2 production via steam reforming reaction, the catalyst must promote the cleavage of C–C, O–H, and C–H bonds in the oxygenated hydrocarbon reactant (leading to H_2 and CO), and facilitate the water gas shift reaction to remove adsorbed CO from the surface as CO_2, as opposed to the cleavage of C–O bonds (leading to alkanes) [13].

Thermodynamic studies of glycerol steam reforming with the method of Gibbs free energy minimization for hydrogen and/or synthesis gas production [14–16] concluded that high temperature, low pressure, and high water/glycerol ratio favor hydrogen production. Optimal conditions for hydrogen production from glycerol were a temperature of 925–975 K and a water/glycerol ratio of 9–12 at atmospheric pressure. Under these conditions, methane production is minimized and the carbon formation is thermodynamically inhibited. However, the biomass-derived oxygenated compounds typically have low thermal stabilities, associated with their high oxygen contents, making it difficult to process them at such a high temperature. Therefore, it is an important challenge to perform the reforming of glycerol at temperatures lower than conventional gasification of biomass (>900 K). Thus, the selection of a catalyst that promotes steam reforming reaction
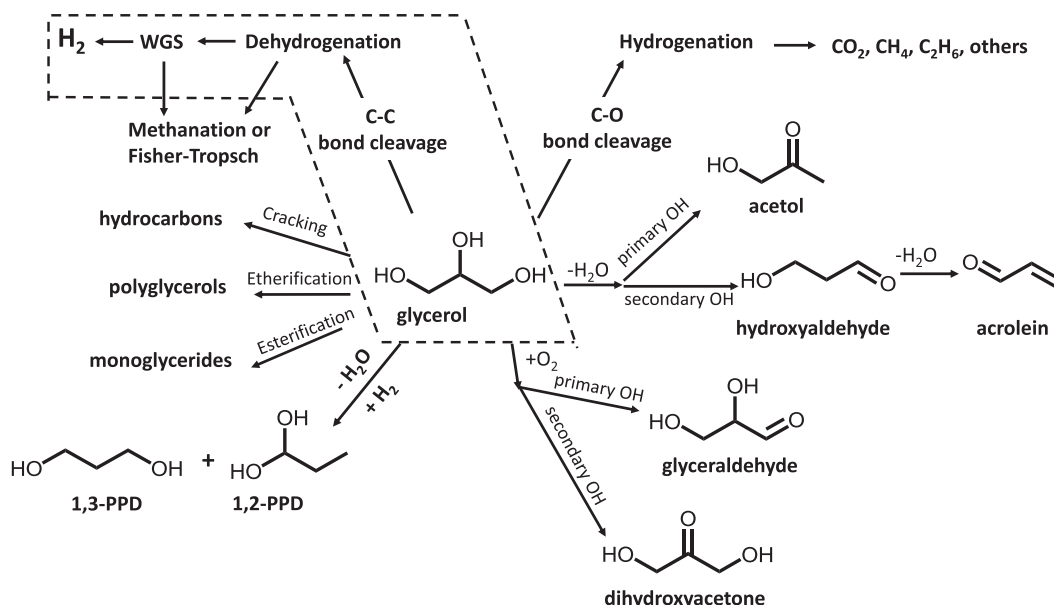

Fig. 1 – Glycerol valorization: different reactions conducting to valuable products.

at low temperature favoring the selective formation of hydrogen is a crucial task. According to literature [17–22], several transition metals (Ru, Rh, Ni, Ir, Co, Pt, Pd and Fe) dispersed on supports are suitable to catalyze steam reforming reaction of biomass-derived oxygenated. Actually, it was reported that the cleavage of C–C bonds as well as C–H and/or O–H bonds to form adsorbed species on the catalyst surface occurs readily over Group VIII metals, mainly Pd and Pt [23]. Pt has been proved to be one of the most active and selective metal for glycerol and ethylene glycol steam reforming due to its capability to break C–C bond and suitability to catalyze the WGS reaction [17,24]. It was also reported that the support plays an important role on catalytic performance of polyols steam reforming [25,26] and water gas shift reaction [27].

We studied in this paper the effect of the nature of the support (acidity, basicity and redox properties) when using Pt-based catalysts in hydrogen production from glycerol by combination of the two reactions involved: glycerol decomposition and WGS. Specifically, we compared the hydrogen yields obtained via steam reforming of glycerol at 623 K over Pt ($\cong$0.5% wt.) supported on silice, alumina, titania and magnesium oxide. We also investigated the effect of the support when using Pt catalysts in WGS reaction at the reaction conditions similar to steam reforming. In order to maximize hydrogen production, we proposed to use a double bed system including the best catalyst for glycerol decomposition and then the most suitable catalyst for improving WGS reaction. Previous results have been reported by Kunkes et al. [28], who using an integrated catalytic system with two beds (5% wt. PtRe/C and 1% wt. Pt/CeO$_2$/ZrO$_2$), have reached a maximum hydrogen yield of 80%. Therefore, the objective of the present study is to explore the effect of the nature of the support for Pt-based catalysts tested in the steam reforming of glycerol (10% wt. glycerol) and water gas shift reaction to maximize the hydrogen yield.

Experimental

Catalyst preparation

Two sets of Pt catalysts were prepared to be tested in both glycerol steam reforming (Group I) and WGS reaction (Group II). The first group of Pt-supported samples (Pt nominal 0.5% wt.) were prepared by incipient-wetness impregnation at 303 K of SiO$_2$ (Grace G62, 99.7%), γ-Al$_2$O$_3$ (Cyanamid Ketjen CK300), TiO$_2$ (Hombifine N, Sachtleben Chemie) and MgO. The oxide magnesium sample was prepared by hydration of commercial MgO (Carlo Erba, 99%, 27 m^2/g) in order to increase the support specific area. Distilled water (50 cm^3) were slowly added to 5 g of commercial MgO and stirred at room temperature; the temperature was then raised to 353 K and stirring was maintained for 3 h. Sample was drying in an oven at 358 K overnight and the resulting Mg(OH)$_2$ was decomposed in N$_2$ flow at 773 K to obtain MgO. Prior to impregnation with Pt salts, all the supports, excepting MgO, were treated in air at 773 K during 4 h. Four Pt-based catalysts were prepared by using H$_2$PtCl$_6$.6H$_2$O solution (Aldrich 99.995%): Pt/SiO$_2$–I, Pt/Al$_2$O$_3$, Pt/TiO$_2$ and Pt/MgO. The Pt/SiO$_2$-II sample was prepared

with the same SiO$_2$ support but using a chloride-free impregnation aqueous solution (tetramine platinum nitrate, Pt(NH$_3$)$_4$(NO$_3$)$_2$, Aldrich, 99.99%). The second group of catalysts includes Pt supported on CeO$_2$ (Rhodia HSA5) and ZrO$_2$ together with Pt/SiO$_2$-II and Pt/TiO$_2$ prepared as descripted above. ZrO$_2$ support was prepared by sol–gel method [29]; the precursor Zr(OC$_3$H$_7$)$_4$ (70% in 1-propanol, Aldrich) was dissolved in 100 cm^3 of isopropyl alcohol and was slowly added (1 cm^3/min) at 305 K to 100 cm^3 of distilled water stirred at 500 rpm. CeO$_2$ and ZrO$_2$ supports were dried overnight at 393 K and treated in flowing air at 873 K for 4 h. Pt-supported samples were prepared by incipient-wetness impregnation of supports at 303 K with aqueous solutions of Pt(NH$_3$)$_4$(NO$_3$)$_2$ (Aldrich, 99.99%). After impregnation, these two samples were dried overnight at 363 K and then treated in dry air at 723 K for 3 h.

Catalyst characterization

BET surface areas (S$_{BET}$) were measured by N$_2$ physisorption at its normal boiling point in a Quantochrome Corporation NOVA-1000 sorptometer. The Pt loadings were measured by atomic absorption spectroscopy.

The platinum dispersion (D$_{Pt}$) of Pt supported on SiO$_2$, Al$_2$O$_3$, MgO, TiO$_2$ and ZrO$_2$ was determined by irreversible H$_2$ chemisorption at 298 K in a conventional vacuum instrument equipped with an MKS Baratron pressure gauge and using the double isotherm method [30]. Catalysts (0.1 g) were reduced in H$_2$ at 573 K for 2 h and then outgassed for 2 h at 623 K except Pt/TiO$_2$ that was outgassed at 573 K to avoid SMSI (strong metal-support interaction) prior to performing gas chemisorption experiments. The hydrogen uptake on Pt/CeO$_2$ was measured by performing H$_2$ pulses at 223 K in order to minimize the atomic hydrogen migration to the support [31] using a Micromeritics AutoChem II 2920 unit. Sample (0.15 g) was reduced in H$_2$ at 673 K, flushed with Ar at 673 K for 30 min and then cooled to 223 K in Ar. The H$_2$ uptake measurements were performed at 223 K by injecting consecutive pulses containing 0.025 cm^3 of H$_2$ in a H$_2$/Ar stream. In all the cases, an atomic H/Pt$_s$ = 1 ratio, where Pt$_s$ implies a Pt atom on surface, was used to calculate D$_{Pt}$.

Sample acidity was characterized by temperature-programmed desorption (TPD) of NH$_3$ in order to estimate the total amount of acid sites. Samples (0.15 g) were treated at 723 K for 2 h in He (60 cm^3/min) and then exposed to a 1% NH$_3$/He stream at 373 K for 40 min. Weakly adsorbed NH$_3$ was removed by flushing with He at 373 K (2 h). The temperature was then increased at 10 K/min and the NH$_3$ concentration in the effluent was measured by using mass spectrometry (Baltzers Omnistar unit). Sample basicity was determined by temperature-programmed desorption (TPD) of CO$_2$ pre-adsorbed at 298 K. Samples (0.15 g) were treated in N$_2$ at 673 K for 1 h and then exposed to a 3% CO$_2$/N$_2$ stream until saturation coverages were reached. Weakly adsorbed CO$_2$ was removed by flushing with N$_2$ at room temperature for 1 h. The temperature was then increased up to 673 K (10 K/min). The desorbed CO$_2$ was converted to methane by means of a methanation catalyst (Ni/Kieselghur) operating at 673 K and monitored using an SRI 8610C gas cromatograph with a flame ionization detector.

Coke formed on the catalysts during reaction was measured by temperature programmed oxidation (TPO) using a 2% O_2/N_2 molar stream as descripted elsewhere [32]. Samples (0.05 g) used in reaction and stabilized at reaction temperature for 45 min in He flow, were heated from 298 K to 1073 K (10 K/min). The evolved CO_2 by oxidation of carbonaceous deposits was converted to methane passing through a methanation catalyst (Ni/Kieselghur) operating at 673 K. Methane was detected and quantified in an SRI 8610C gas cromatograph equipped with a flame ionization detector.

Catalytic activity

The steam reforming reaction of glycerol was carried out in a fixed bed reactor at atmospheric pressure and moderates temperatures (573–623 K). Samples (0.2 g, particles size 0.35–0.42 mm) were treated with pure H_2 (75 cm^3/min) in-situ, at 623 K for 1 h before reaction in order to reduce all Pt. A 10% wt. glycerol (99.5+%; Sigma Aldrich) aqueous solution was introduced into the reactor using a syringe pump (Cole Palmer, 74900) and vaporized into flowing He (6 cm^3/min). A typical reaction was conducted at a contact time of 46 g h/mol glycerol and partial pressures of $P_{H2O} = 94.6$ kPa, $P_G = 2$ kPa and $P_{He} = 4.7$ kPa. The effluent from reactor was cooled by passing through a condensation system and then conducted to a gas–liquid separator where condensable products were drained periodically and quantified by using an Agilent 6850 gas chromatograph equipped with a flame ionization detector and a 30 m Innowax column (inner diameter: 0.32 mm, film thickness: 0.5 μ). An aqueous solution of 2-propanol (Sigma-Aldrich, 99.5%) was used as external standard to calculate glycerol conversion. The gas products (H_2, CO, CO_2 and CH_4) were analyzed on-line in an HP 5890 gas chromatograph equipped with a thermal conductivity detector and a Hayesep D 100-120 column (5 m × 1/8 in × 2.1 mm) using He as gas carrier. Both liquid and gas samples were collected and analyzed every 15 min during 3 h. The carbon based total conversion of glycerol (X_G^t) was calculated according to Equation (1) and accounts for the moles of glycerol (in carbon basis) converted to both gaseous and liquid products. The conversion of glycerol to gaseous products (X_G^g) accounts for the amount of glycerol transformed into gaseous products containing carbon atoms of the feed, i.e. CO, CO_2 and CH_4 (Equation (2)). Hydrogen yield (η_{H2}) is defined in Equation (3) where R is the H_2/CO_2 reforming ratio of 7/3 for glycerol. This η_{H2} definition takes into account that $4H_2$ molecules come from one molecule of glycerol whereas 3 molecules of H_2 proceed from water.

$$X_G^t = \frac{F_G^I - F_G}{F_G^I} \times 100 \tag{1}$$

$$X_G^g = \frac{\sum \alpha_i \cdot F_i}{\alpha_G \cdot F_G^I} \times 100 \tag{2}$$

$$\eta_{H2} = \frac{F_{H2}}{F_G^I} \times \frac{1}{R} \times 100 \tag{3}$$

where α_G are the number of C atoms in the glycerol molecule, F_G^I and F_G are the glycerol molar flow at the inlet and the exit of the reactor, respectevely, α_i are the number of C atoms in the product i molecule, F_i is the molar flow of gaseous product i formed from glycerol and F_{H2} is the molar flow of H_2.

The WGS reaction was carried out in a pyrex plug-flow fixed-bed reactor (0.8 cm ID) at 623 K and 101.3 kPa feeding a mixture H_2O and CO ($P_{CO} = 3$ kPa, $P_{H2O} = 9$ kPa) balanced with He. Prior to catalytic tests, samples were reduced in pure H_2 at 623 K for 1 h. On-line chromatographic analysis was performed using a gas chromatograph SRI 310C equipped with a flame ionization detector and a silica gel column. Before gas chromatographic analysis, the reaction products were separated and CO and CO_2 completely converted to CH_4 by means of a methanation catalyst (Ni/Kieselghur) operating at 673 K. Carbon monoxide conversion (X_{CO}) was calculated as $X_{CO} = Y_{CO2}/(Y_{CO} + Y_{CO2}) \times 100$ where Y_{CO} and Y_{CO2} are the molar fraction of CO and CO_2 at the exit of the reactor, respectively.

Results and discussion

Catalysts characterization

In order to investigate the effect of the nature of the support over glycerol steam reforming reaction, we prepared Pt catalysts using several solids with different physical and chemical properties: SiO_2, Al_2O_3, TiO_2 and MgO. Pt/CeO_2 and Pt/ZrO_2 were additionally prepared and characterized to be tested in WGS reaction. The physicochemical and acid/basic properties of these samples are shown in Table 1. The surface area (S_{BET}) of the supports remained almost invariant after impregnation with Pt solution. The surface areas for all the catalysts, except Pt/MgO and Pt/ZrO_2, were higher than 175 m^2/g. The Pt dispersions (D_{Pt}) determined by H_2 chemisorption at 298 K were about 35–50 % for all the catalysts, excepting Pt/TiO_2 and Pt/ZrO_2.

The acidic properties of the samples were analyzed by temperature programmed desorption of previously adsorbed NH_3. Pt/TiO_2 showed the highest acid site density followed by Pt/Al_2O_3 (173 and 118 μmol NH_3/g respectively). Although the silica employed as support is not acid at all, Pt/SiO_2–I sample showed a very small NH_3 desorption peak attributed to the acidity caused by the residual chlorine which comes from the solution used to perform the impregnation [33]. Pt/SiO_2-II, prepared by using a chlorine-free solution, did not exhibit any peak in NH_3 TPD profile. The basicity of samples were studied by temperature programmed desorption of CO_2 preadsorbed at room temperature. The total basic site densities were determined by integration of TPD curves and reported as μmol/g in Table 1. As expected, Pt/MgO displayed the highest basicity (479 μmol CO_2/g). Pt/TiO_2 and Pt/Al_2O_3 showed small CO_2 desorption peaks (35–18 μmol CO_2/g).

Glycerol steam reforming

Effect of reaction temperature over glycerol conversion and product selectivities

Glycerol and water may react to produce H_2, CO, CO_2, CH_4 and some condensable products formed by reactions of dehydration, dehydrogenation, hydrogenolysis, among others, of glycerol or derivatives thereof such as acetol, acrolein,

Table 1 – Catalysts characterization.

Catalyst	Pt loading (% wt.)	S_{BET} support (m^2/g)	S_{BET} catalyst (m^2/g)	Pt dispersion (%)	NH_3 TPD (µmol/g)	CO_2 TPD (µmol/g)
Pt/SiO$_2$-I	0.48	230	225	42	8	–
Pt/Al$_2$O$_3$	0.47	180	175	45	118	18
Pt/TiO$_2$	0.50	186	180	11	173	35
Pt/MgO	0.49	106	108	35	18	479
Pt/SiO$_2$-II	0.50	230	227	38	0	–
Pt/CeO$_2$	0.40	260	242	49	–	–
Pt/ZrO$_2$	0.48	51	45	73	–	–

acetaldehyde and 1,2-propanediol. With the aim of selecting the most appropriate reaction temperature for the selective formation of H$_2$, the influence of this parameter on the glycerol total conversion, X_G^t, glycerol to gaseous products conversion, X_G^g, and gaseous products distribution was studied using Pt/SiO$_2$-I; results at 573, 598 and 623 K are shown in Fig. 2. The initial X_G^t was about 90–100% for the range of temperature tested here and decreased with time on stream (X_G^t = 30, 39 and 50% for 573, 598 and 623 K respectively after 3 h of reaction). The conversion of glycerol to gaseous products showed a similar tendency: it was about 40–60% initially but after 3 h reaction decay up to 25–39 %. The molar gas phase composition remained invariant during reaction in spite of the deactivation noticed. H$_2$ was the main component within gas-phase products (55–60 % molar) and CH$_4$ formation was very low (1–2% molar) in all the cases. It is important to remark here that the maximum H$_2$ molar fraction possible is 70% according to the stoichiometry of Reactions (1)–(3). CO concentration for the lowest reaction temperature (573 K) was 40% molar whereas the CO$_2$ formation was low (4% molar) at such temperature. However, after increasing 50 K, CO$_2$ concentration increased to 20% at the expense of CO, whose concentration decreased to 22%; in addition, the highest H$_2$ concentration was obtained at 623 K. Thus, the highest temperature tested here (623 K) seems to be the most suitable for reaching high H$_2$ yields by improving both the glycerol conversion to gas phase products and H$_2$ selectivity. We chose 623 K as the most appropriate temperature and we study the effect of the nature of the support as follow.

Effect of the support on H$_2$ production

We compare glycerol conversion and gas-phase composition at identical reaction conditions (Table 2, rows 1–4) for the four catalysts of Pt prepared from H$_2$PtCl$_6$ aqueous solution and using different supports (SiO$_2$, Al$_2$O$_3$, TiO$_2$ and MgO). MgO is a basic solid whereas Al$_2$O$_3$ and TiO$_2$ were the most acidic supports used here (Table 1). In addition, TiO$_2$ has well-known redox properties which can be useful to catalyze WGS reaction and it was actually selected to be tested in steam reforming of glycerol because of this capability. The four catalysts (Pt/SiO$_2$-I, Pt/Al$_2$O$_3$, Pt/TiO$_2$ and Pt/MgO) showed initial X_G^t $\cong$ 95–100%. Pt/SiO$_2$-I and Pt/MgO significantly favored the conversion of glycerol to gaseous products (X_G^g = 60%) and consequently the production of H$_2$ (η_{H2} = 38.6 and 41.9% respectively). On the other hand, when Pt is supported on acid solids such as Al$_2$O$_3$ and TiO$_2$, significant amounts of glycerol were consumed in undesirable side reactions such as dehydrations and dehydrogenations catalyzed by the presence of acid sites leading to low X_G^g (10 and 20%, respectively). Acrolein, acetol, 1,2-propanediol, acetic acid and acetaldehyde were the main liquid products formed when using Pt/Al$_2$O$_3$ and Pt/TiO$_2$ in good agreement with literature [25]. In all the cases, H$_2$ was the main product among gas products followed by CO; CO$_2$ was formed as a product of WGS reaction while insignificant amounts of methane were detected proving that methanation reaction is not favored in the conditions of the present research. Pt/TiO$_2$ sample was the most active catalyst for the WGS reaction, as it is shown in Section Study of water gas shift reaction using Pt catalysts; however, the glycerol conversion
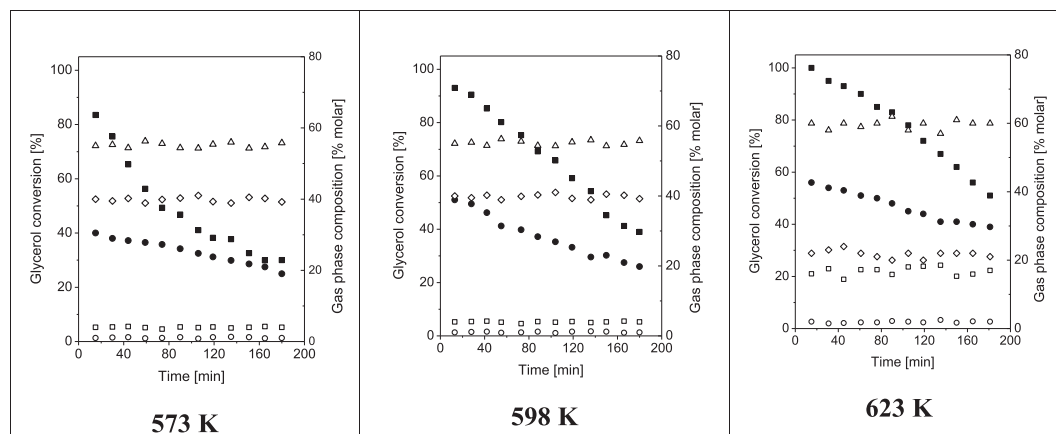
Fig. 2 – Glycerol conversion and gas phase molar composition as a function of time-on-stream for different reaction temperatures on 0.48% wt. Pt/SiO$_2$-I [46 g h/mol glycerol, 10% wt. glycerol, P_T = 101.3 kPa, P_{H2O} = 94.6 kPa, P_G = 2 kPa, P_{He} = 4.7 kPa]. Glycerol conversions: X_G^t (■), X_G^g (●), molar gas phase composition: H$_2$ (△), CO (◇), CO$_2$ (□), CH$_4$ (○).

Table 2 – Glycerol conversion and H$_2$ yield for Pt on different supports.

Catalyst	X_G^t (t = 0)	X_G^g (t = 0)	% Molar gas phase				η_{H2}
			H$_2$	CO	CO$_2$	CH$_4$	
Pt/SiO$_2$-I	100	60	60	22	16	2	38.6
Pt/Al$_2$O$_3$	100	10	59	23	16	2	6.17
Pt/TiO$_2$	100	20	62	20	18	0	14.0
Pt/MgO	95	60	62	23	14	1	41.9
Pt/SiO$_2$-II	100	99	65	7	26	2	78.8

623 K, 46 g h/mol glycerol, 10% wt. glycerol, P_T = 101.3 kPa, P_{H2O} = 94.6 kPa, P_G = 2 kPa, P_{He} = 4.7 kPa.

to gas products (X_G^g) on this solid was low because the acidity of this support promotes the formation of undesirable liquid products. Thus, Pt/TiO$_2$ catalyst was not useful for the selective formation of H$_2$ from glycerol because did not selectively promote the decomposition reaction of glycerol (C–C bond cleavage) which is a previous step to the WGS reaction.

The relationship between the acidity of the support and the production of undesirable liquid compounds and the previous knowledge that the presence of residual chlorine from the solution used for impregnating the catalyst confer acidic properties to the catalyst [33], motivated us to synthesize a chlorine-free catalyst (Pt/SiO$_2$-II) by employing Pt(NH$_3$)$_4$(NO$_3$)$_2$ as precursor; the absence of acidity was corroborated by TPD of NH$_3$ (Table 1). When testing Pt/SiO$_2$-II in steam reforming reaction, both the initial total glycerol conversion and initial conversion to gaseous products were almost 100% (Table 2, last row). The H$_2$ yield was 78.8%, the highest value reported in Table 2. These results showed that Pt/SiO$_2$-II sample was the most suitable catalyst to produce H$_2$ from glycerol and water. Pt supported over an inert solid 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 CO$_2$ that produce light alkanes. It is important to remark that the SiO$_2$ used here did not show neither basic nor acid properties and was not active for steam reforming reaction either. Actually, we have tested the glycerol reforming reaction on SiO$_2$ and no conversion of glycerol was noticed. Our results are in good agreement with the information available in literature suggesting that the selection of a non-acidic support is appropriate to syn-gas and/or hydrogen production via steam reforming reaction of several oxygenates compounds derived from biomass [25,34,17].
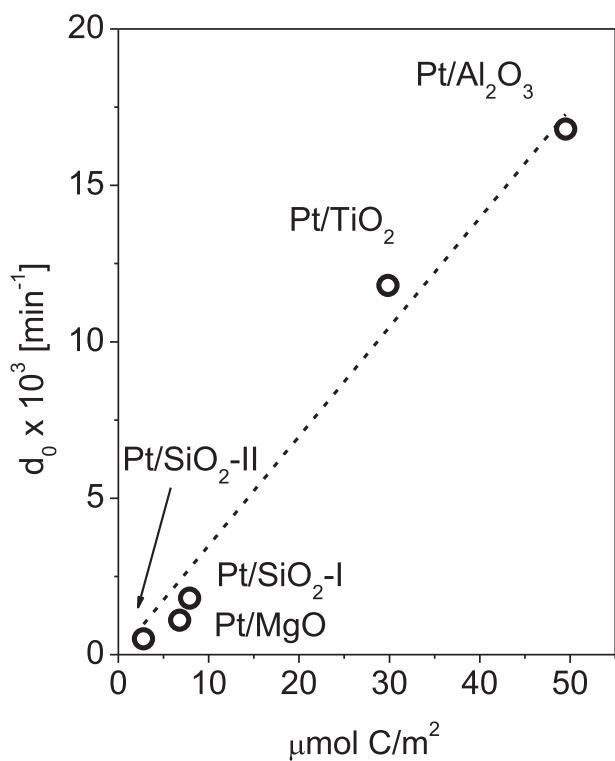
Catalysts deactivation and coke formation
We have observed in our experiments that glycerol to gas-phase products conversion (X_G^g) decreased with time. Other authors [17], that have also reported deactivation during steam reforming of glycerol, have indicated that the support plays an important role in this deactivation process. In order to compare the activity decay of the different Pt-based catalysts during glycerol steam reforming, we showed in Fig. 3 the activity a_G as a function of time on stream; a_G is defined as $a_G = r_G/r_G^0$, where r_G^0 and r_G are the glycerol to gas-phase products conversion rates at t = 0 and t = t, respectively. From the initial slopes of activity versus time curves it was

calculated the d_0 parameter as $d_0 = -[da_G/dt]_{t=0}$ accounting for initial deactivation rate. As it can be observed in Fig. 3, Pt/SiO$_2$-II was the most stable catalyst during steam reforming reaction. In fact, the lowest d_0 value was obtained on this catalyst, while Pt/Al$_2$O$_3$ and Pt/TiO$_2$ catalysts presented the highest initial deactivation, more than one order of magnitude higher than those for Pt supported over non-acidic solid (d_0 values were 0.0168, 0.0118 and 5×10^{-4} min^{-1} for Pt/Al$_2$O$_3$, Pt/TiO$_2$ and Pt/SiO$_2$-II respectively).

Sample deactivation could be caused by blockage of the active sites due to coke formation. Actually, it was reported [17] that catalyst deactivation would be caused by dehydration on the oxide catalyst supports, which leads to the formation of unsaturated hydrocarbon species that form carbonaceous deposits on the Pt surface, thereby decreasing the rate of H$_2$ production. Therefore, the samples tested in reaction were recovered and analyzed by TPO technique. The amount of coke formed (mol C/g catalyst) was determined by integration of the oxidation profiles. We also calculated the mol of carbon per m^2 of surface area (mol C/m^2) as the mol C/g catalyst divided by the S_{BET} showed in Table 1. In Fig. 4 we plotted the initial deactivation (d_0) determined from Fig. 3 as a function of the carbon formation (reported as mol C/m^2). A linear tendency was achieved indicating that catalyst deactivation is caused by coke formation. Indeed, the carbon content for Pt/Al$_2$O$_3$ and Pt/TiO$_2$ samples were 49.5 and 29.8 μmol C/m^2, respectively, and they presented the highest initial deactivation rate. On the other hand, the less acidic sample, Pt/SiO$_2$-II displayed almost no deactivation during reaction and formed the lowest amount of coke (2.8 μmol C/m^2). Consequently, the
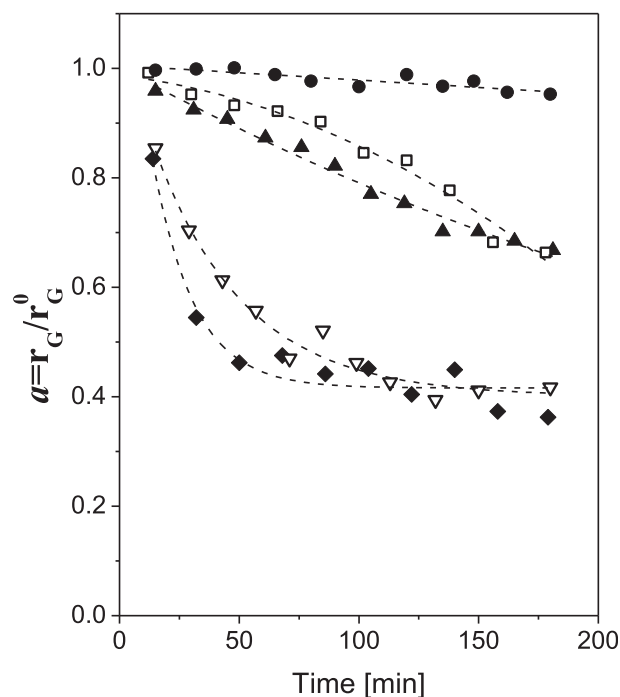
Fig. 3 – Time evolution of the activity for glycerol to gas phase products conversion (a$_G$) on Pt-based catalysts [Pt/SiO$_2$-II (●), Pt/MgO (□), Pt/SiO$_2$–I (▲), Pt/TiO$_2$ (▽) and Pt/Al$_2$O$_3$ (◆), 623 K, 46 g h/mol glycerol, 10% wt. glycerol, P_T = 101.3 kPa, P_{H2O} = 94.6 kPa, P_G = 2 kPa, P_{He} = 4.7 kPa].

Fig. 4 – Initial catalyst deactivation (d_0) as a function of the amount of coke formed during reaction.

acidity of the support seems to be related to the catalyst deactivation and the coke formation during reaction in good agreement with the widely accepted concept that acid sites catalyze reactions conducting to the formation of coke precursors. Thus, we conclude that the catalyst deactivation is mostly caused by blockage of the active sites by coke precursors formed on surface acid sites. Moreover, an important difference on deactivation and coke formation between the Pt/SiO$_2$-I and Pt/SiO$_2$-II was observed, showing that the election of Pt-precursor is very important to get a more active and stable catalyst. In summary, Pt/SiO$_2$-II efficiently improves glycerol conversion to gaseous products and hydrogen yield while minimizes the coke formation.

*Study of water gas shift reaction using Pt catalysts*

Significant amounts of CO (23-7 % molar in gas-phase products, Table 2) were formed during glycerol steam reforming experiments, indicating that WGS reaction was not operating at the equilibrium condition (X_{CO}^{eq} = 100% [35,36]). This result motivated the idea of adding a second bed to integrate the glycerol steam reforming and water gas shift processes in a single reactor system operating at the same temperature. Therefore, the WGS catalyst must be active and stable at intermediate temperatures, at which Cu-based WGS catalysts tend to sinter and Fe-based WGS catalysts display low activity. Numerous investigators have observed that oxide-supported noble metal catalysts may offer significant advantages to Cu-based catalysts, including operation at higher temperatures and greater resistance to sintering [17,37–40].

Accordingly, we studied the WGS performance of platinum supported catalysts at the steam reforming temperature (623 K). We choose simple oxides as supports (non-reducible: SiO$_2$ and reducible: TiO$_2$, CeO$_2$ and ZrO$_2$) and prepared Pt/support catalysts by incipient-wetness impregnation as reported in Section Catalyst preparation. It is well known that Pt/CeO$_2$, Pt/TiO$_2$ and Pt/ZrO$_2$ are suitable to catalyze water gas shift reaction at moderate reaction temperatures (473–623 K) [41–44]. Moreover, Pt supported on TiO$_2$ has shown better activity towards the low-temperature WGS reaction (523 K) compared to other reducible oxides such as CeO$_2$, ZrO$_2$, and their mixed oxides [27]. We also tested Pt/SiO$_2$-II due to its very good performance in glycerol decomposition as reported in Table 2.

Catalytic results of WGS reaction are shown in Fig. 5 as CO conversion (X_{CO}) versus time on stream feeding an excess of water (P_{CO} = 3 kPa, P_{H2O} = 9 kPa, balance He). CO conversion for all the catalysts slightly decreased during the first 60 min of reaction and then reached a stationary state. As expected, Pt/SiO$_2$-II was the less active catalyst tested here [27,45]. CO conversion rate followed the order: Pt/TiO$_2$ > Pt/ZrO$_2$ > Pt/CeO$_2$ » Pt/SiO$_2$-II. According to literature, the WGS reaction is promoted on Pt-based catalysts via metallic monofunctional or metal-support bifunctional mechanisms depending on the reducibility of support [27]. Platinum supported on non-reducible SiO$_2$ catalyzes the WGS reaction through a monofunctional redox mechanism involving the adsorption and activation of reactants, CO and water, on the metallic fraction. Therefore, the activity for the WGS reaction on Pt-based catalysts is highly influenced by the nature of the support,
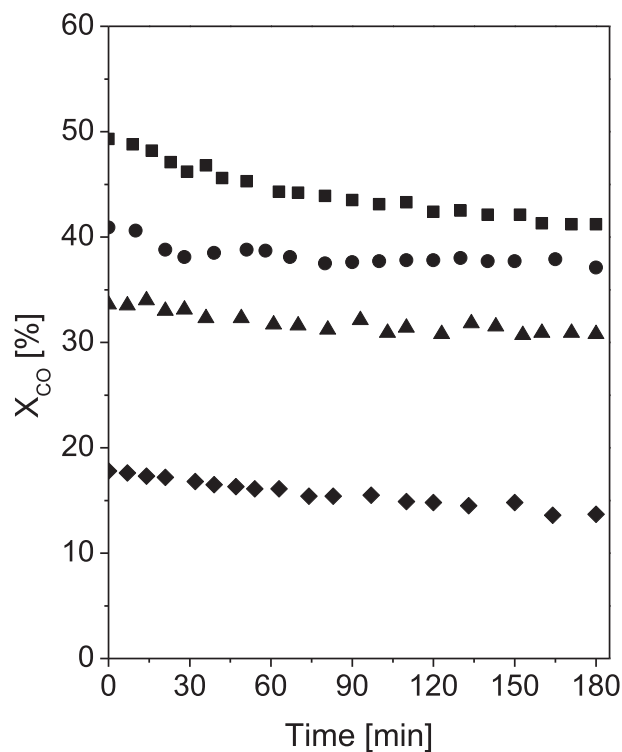
Fig. 5 – CO conversion during water gas shift reaction over Pt-based catalysts [Pt/TiO$_2$ (■), Pt/ZrO$_2$ (●), Pt/CeO$_2$ (▲) and Pt/SiO$_2$-II (◆), 623 K, 2.17 g h/mol CO, P_T = 101.3 kPa, P_{CO} = 3 kPa, P_{H2O} = 9 kPa, P_{He} = 89.3 kPa].
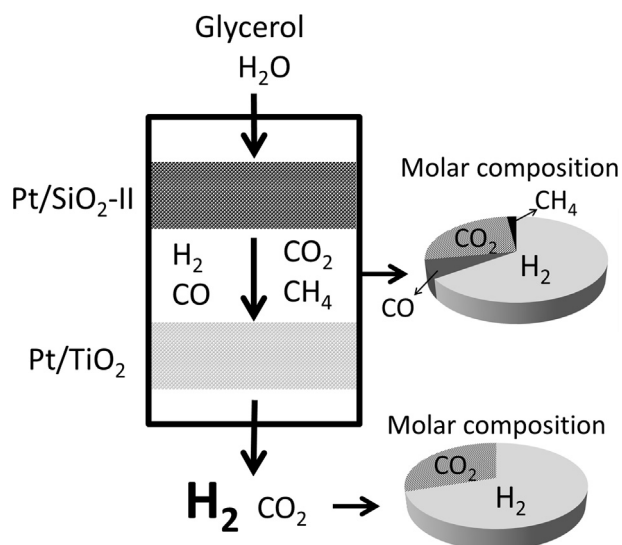
Fig. 6 – Double bed system for maximizing the hydrogen production.

essentially because the reaction intermediate and pathways occurring on the support in the bifunctional metal-support mechanism greatly depend on the support redox properties. The high CO conversion obtained on Pt/TiO$_2$ (Fig. 5) is in good agreement with results previously informed in literature at lower temperature (303–573 K) [27]. Therefore, we selected the 0.5% wt. Pt/TiO$_2$ catalyst as the most active sample to improve hydrogen formation from CO and water at 623 K.

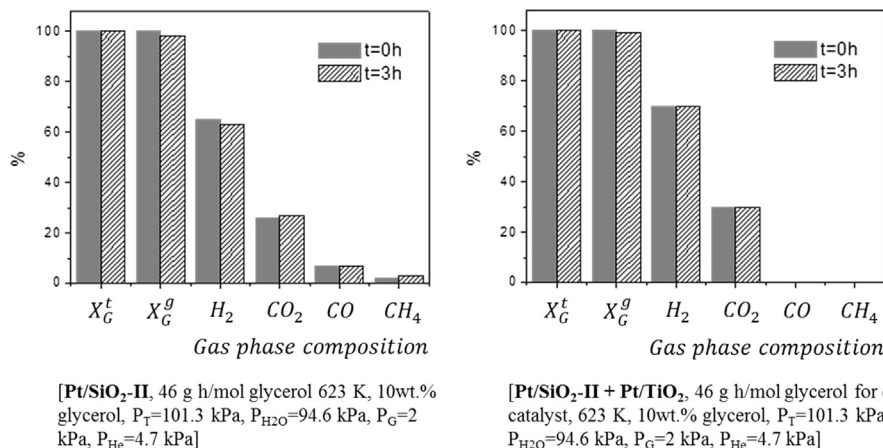### Integrated glycerol steam reforming and water gas shift reaction

Results from Table 2 and Fig. 3 suggest that Pt/SiO$_2$-II is the most active and stable catalyst for glycerol decomposition to gas products. In order to increase the H$_2$ selectivity and reduce the CO content, we decided to add a second catalyst that favors WGS reaction. According to results informed in Fig. 5, Pt/TiO$_2$ is the most suitable catalyst for this step. Thus, a two beds system

(Fig. 6) formed by a first catalyst that favors glycerol decomposition (Pt/SiO$_2$-II) and a second catalyst that promotes WGS reaction (Pt/TiO$_2$), was tested in the glycerol to H$_2$ conversion. Both catalysts were placed consecutively in the same reactor, operating at the same reaction temperature (623 K).

Fig. 7 shows the conversion of glycerol (X_G^t and X_G^g), hydrogen yield and molar composition of the gas phase when using 0.5% wt. Pt/SiO$_2$-II (Fig. 7A) and the double bed system (Fig. 7B). In both cases, neither glycerol nor liquid products were detected in the exit of the reactor indicating that glycerol was totally converted to gas phase products (X_G^g = 100%). Although glycerol is selectively transformed to gas products when using only Pt/SiO$_2$-II, considerable amounts of CO is still present indicating that WGS reaction did not reach the equilibrium. After adding the second catalyst (Pt/TiO$_2$), we showed in Fig. 7 that the amount of H$_2$ formed was the maximum possible (70% molar fraction) according to the stoichiometry of the Reactions (1) and (2) conducting at a 100% of hydrogen yield. Additionally, the dual system showed no deactivation during 3 h reaction. Kunkes et al. [28] have previously reported that hydrogen yields of about 80% are achieved using a two-bed system formed by a first bed of 5% wt. Pt/C or 5% wt. Pt–Re/C and a second bed of 1% wt. Pt/CeO$_2$–ZrO$_2$. The results shown in this paper prove that Pt supported on SiO$_2$ and TiO$_2$ in amounts as low as 0.5% wt. may efficiently catalyze the glycerol steam reforming and WGS to get 100% H$_2$ yield at 623 K.

Conclusions

Glycerol steam reforming reaction is an interesting way to produce eco-friendly hydrogen. The catalyst involved must be able to cleavage of C–C, O–H, and C–H bonds in the oxygenated reactant and prevent C–O scissions conducting to undesirable liquid products. In this sense, Pt is a good alternative but the election of the support is a crucial task. This research shows that catalysts based on Pt, even containing as low amount of noble metal as 0.4–0.5% wt., are suitable to reach 100% hydrogen yield when feeding a 10% wt. glycerol aqueous solution at 623 K.

[**Pt/SiO$_2$-II**, 46 g h/mol glycerol 623 K, 10wt.% glycerol, P$_T$=101.3 kPa, P$_{H2O}$=94.6 kPa, P$_G$=2 kPa, P$_{He}$=4.7 kPa]

[**Pt/SiO$_2$-II + Pt/TiO$_2$**, 46 g h/mol glycerol for each catalyst, 623 K, 10wt.% glycerol, P$_T$=101.3 kPa, P$_{H2O}$=94.6 kPa, P$_G$=2 kPa, P$_{He}$=4.7 kPa]

Fig. 7 – Glycerol conversion, gas phase composition and hydrogen yield for a single-bed and double-bed system. A: [Pt/SiO$_2$-II, 46 g h/mol glycerol 623 K, 10% wt. glycerol, P$_T$ = 101.3 kPa, P$_{H2O}$ = 94.6 kPa, P$_G$ = 2 kPa, P$_{He}$ = 4.7 kPa]. B: [Pt/SiO$_2$-II + Pt/TiO$_2$, 46 g h/mol glycerol for each catalyst, 623 K, 10% wt. glycerol, P$_T$ = 101.3 kPa, P$_{H2O}$ = 94.6 kPa, P$_G$ = 2 kPa, P$_{He}$ = 4.7 kPa].

Glycerol decomposes over Pt catalyst to form CO and H_2; then in a consecutive step, the CO formed may react with water present in excess to render more H_2 and CO_2. In order to maximize the hydrogen production, we studied separately the two reactions involved: i) glycerol decomposition using Pt supported over solid with different physicochemical and acid–basic properties (i.e. SiO_2, MgO, Al_2O_3 and TiO_2), and ii) WGS reaction testing Pt supported over simple oxides (SiO_2, TiO_2, CeO_2 and ZrO_2). Pt/SiO_2-II prepared from a chlorine-free precursor solution showed the highest H_2 yield within the first series of catalyst (η_{H2} = 78.8%). Acid supports greatly favor parallel reactions such as dehydrogenation, dehydration, etc. from glycerol conducting to undesirable products and causing catalyst deactivation. Studies of WGS reaction at temperatures compatible with glycerol steam reforming, i.e. 623 K, shows that Pt/TiO_2 efficiently catalyze this step, even without extra H_2 in the feed. In order to maximize the H_2 production, both catalysts (0.5% wt. Pt/SiO_2-II and 0.5% wt. Pt/TiO_2) were placed in the reactor separated from each other and operating at the same temperature. This double-bed system allows to get the maximum hydrogen yield possible (η_{H2} = 100%) without deactivation on stream.

Acknowledgments

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