Renewable H₂ from glycerol steam reforming: effect of La₂O₃ and CeO₂ addition to Pt/Al₂O₃ catalysts.


Glycerol is the main by-product of biodiesel production and its exceeding production derives to the more and more increasing biofuels demand. Therefore, glycerol conversion to H₂-rich mixtures is not only an interesting research topic but more importantly an attractive way towards a sustainable biodiesel production. Here we explored the use of Pt/Al₂O₃-based catalysts for the catalytic steam reforming of glycerol, evidencing the influence of La₂O₃ or CeO₂ doping on the catalyst activity and selectivity. The addition of the latter metal oxides to a Pt/Al₂O₃ catalyst is found to significantly improve the glycerol steam reforming, with high H₂ and CO₂ productions. A good catalytic stability is finally achieved for the Pt/La₂O₃/Al₂O₃ system working at 350 °C, while the Pt/CeO₂/Al₂O₃ catalyst sharply deactivates after 20 h under similar conditions. Studies carried out on fresh and exhaust catalysts have revealed that both systems maintain high surface area and high Pt dispersion. Therefore, the observed catalyst deactivation can be attributed to coke deposition on the catalyst active sites throughout the catalytic process and marginally to the Pt nanoparticle sintering. This work suggests that an appropriate support composition is of mandatory importance for preparing highly performing Pt-based catalysts for the sustainable glycerol conversion into syn-gas.

Introduction

The use of renewables, such as biomasses, is essential for a sustainable development of our society. The conversion of renewable resources into either clean fuels or chemicals is attracting growing interests due to the continuous reduction of fossil hydrocarbons supplies.[1] Depending on the starting biomass-based material, the fuel production can result significantly or not. First generation bio-fuels are essentially composed by ethanol and biodiesel, obtained from sugar fermentation and transesterification of animal fats or vegetable oils, respectively. Unfortunately, the production of these biofuels is not sustainable on a long term period because it can seriously compromise both food supplies and biodiversity. The use of biomasses consisting of residual non-food parts of current crops represents a challenging goal for the sustainable production of second generation biofuels, whose production can start from the extraction of complex molecules, such as lignin or cellulose, from woods or fibrous biomasses. To this purpose, several catalytic processes for the production of useful chemicals and feedstocks via hydrolysis of lignocellulose residues have been already investigated.² Third generation biofuels can be finally produced from marine biomasses, such as algae, with higher energy balances than those obtained from land crops.

In this contest, hydrogen is asked to play an important role in the conversion of chemical industry towards the increasing use of renewable sources. In fact, hydrogen is not only a fundamental chemical for important industrial processes but it is also considered an attractive and clean energy vector in the timely fuel cells technology.[1] Nowadays hydrogen is mostly used for fuel purification from sulfur and nitrogen (HDS and HDN steps), ammonia synthesis, cracking / refining processes, methanol production, hydrogenation reactions, fuel production via Fisher-
Tropsh synthesis as well as many other industrially relevant processes.\textsuperscript{[6]} In the energy field, hydrogen is more properly conceived as an energy vector rather than an energy source as its production requires energy from other sources.\textsuperscript{[4,5]} Since the current industrial hydrogen production is essentially based on fossil fuels (~ 90% from methane and ~ 5% from other hydrocarbons), extensive research efforts have been devoted in the last few years to develop new processes for its clean and sustainable production.\textsuperscript{[6-14]}

The implementation of new biorefineries for the valorization of biomasses, especially those obtained from agriculture residues, is considered a successful alternative for the sustainable preparation of chemicals (including H\textsubscript{2}) and biofuels.\textsuperscript{[15-17]} Several methods have been proposed for the H\textsubscript{2} production from renewables, among which biomass reforming and water electrolysis using solar, wind or hydroelectric power.\textsuperscript{[16]} However, solar photocatalytic splitting of water remains ultimately the challenging task for a really sustainable H\textsubscript{2} production.

Recently, biodiesel has become one of the most promising biofuels \textsuperscript{[19-22]} although its high production costs represent the main limitation to its worldwide commercialization. The recovery of by-products deriving from the biodiesel production (mainly glycerol) and their re-use as new feedstocks in biorefineries\textsuperscript{[23,24]} can strongly contribute to cut down the overall biodiesel production costs. Among by-products, glycerol represents both a potential source for obtaining hydrogen and a valuable solution for making the biodiesel production really sustainable.\textsuperscript{[4,5]}

Recent reviews account for a large variety of catalytic and enzymatic transformation of glycerol into surfactants, fuel additives and, more in general, into high-value chemical derivatives.\textsuperscript{[2,25-30]} Although the variety of value-added chemicals those can be obtained from glycerol is wide, the use of this feedstock for obtaining hydrogen has gained a lot of attention due to the expected exponential increase of hydrogen demand, mainly in fuel cells applications.\textsuperscript{[31]}

Glycerol can be converted into syn-gas by Steam Reforming (SR) according to the following reaction:

\[
\text{C}_3\text{H}_5\text{O}_3 + 3\text{H}_2\text{O} \rightarrow 3\text{CO} + 7\text{H}_2 \quad (1)
\]

This process can be formally written also as a combination of two separate reactions: glycerol decomposition into H\textsubscript{2} and CO (Eq. 2) followed by the Water Gas Shift (WGS) equilibrium (Eq. 3):

\[
\text{C}_3\text{H}_5\text{O}_3 \rightarrow 3\text{CO} + 4\text{H}_2 \quad (2)
\]

\[
\text{CO} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2 \quad (3)
\]

Typically, the glycerol SR is a catalytic process that occurs in vapor phase at atmospheric pressure and temperatures up to 900 °C. Due to its endothermicity, high temperatures, low pressures and a high steam-to-glycerol ratio are generally required to get high substrate conversions.\textsuperscript{[31]} Compared to the Aqueous Phase Reforming (APR) protocol, SR requires higher energy to vaporize the biomass solutions. In spite of this general disadvantage, SR could be preferred to the APR protocol because of the lower amount of contaminating side-products produced during the process. Indeed, under SR conditions, the amount of methane and higher hydrocarbon products can be significantly reduced compared to the APR conditions.\textsuperscript{[11,32]} Just simply running the reaction at atmospheric pressure instead of higher pressures as required by the APR process.\textsuperscript{[31]} Finally, the APR process, in case of concentrated solutions, need to be still optimized.\textsuperscript{[11,33]}

Many metal catalysts have been scrutinized for the glycerol SR among which Ru\textsuperscript{[34-36]}, Rh\textsuperscript{[35,37]} Ir\textsuperscript{[35,38-39]}, Pd\textsuperscript{[35,40,41]}, Pt\textsuperscript{[35,37,42-46]} Co\textsuperscript{[46]} and mainly Ni\textsuperscript{[35,38,41,44-46-50]} are the most representative ones. Pt is a good candidate for the glycerol SR allowing for efficient C-C, O-H and C-H bond cleavages with high activity and selectivity levels. On the contrary, other metals need the promoting effect of additional metals to ensure good activities and high H\textsubscript{2} selectivity values.\textsuperscript{[40,43,51]}

A wide variety of supports for the metal active sites have also been tested in the glycerol SR reaction, from acidic supports\textsuperscript{[35]} to basic ones.\textsuperscript{[47]} in many cases without attention to the non innocent role of these materials on the paying performances of the catalytic system.

An effective catalyst for the H\textsubscript{2} production from glycerol is expected to break-up the substrate via C-C, O-H and C-H bond cleavages promoting, at the same time, the elimination of the metal-passivating carbon monoxide via WGS reaction. Finally, such a catalyst should promote neither the C-O cleavage nor the CO or CO\textsubscript{2} hydrogenation to form either alkanes or more polar compounds.\textsuperscript{[52]}

Many research efforts are required to transfer the glycerol SR from lab to industry. Indeed, some important properties of the catalytic system, such as stability and selectivity towards H\textsubscript{2} production, must be carefully considered prior any scale-up. Moreover, catalyst deactivation due to coke deposition on the catalyst surface represents one of the most important limitations to the industrial scale-up of the glycerol SR. It is well known that CeO\textsubscript{2} can act as a non innocent support, preventing, to some extent, the coke deposition at the catalyst active sites by the promotion of redox processes.\textsuperscript{[38,53,54]} Finally, CeO\textsubscript{2} can efficiently catalyze the WGS reaction,\textsuperscript{[38,55-57]} thus eliminating carbon monoxide from the gas phase and preventing the catalysts from passivation/deactivation effects.

It should be pointed out that acidic catalyst supports, such as Al\textsubscript{2}O\textsubscript{3}, can promote the occurrence of side reactions during the SR process basically leading to saturated\textsuperscript{[20]} or unsaturated hydrocarbon\textsuperscript{[58]} products. One possible alternative to control the density of acid sites in these supports is their impregnation with basic oxides such as La\textsubscript{2}O\textsubscript{3} or CeO\textsubscript{2}.

In this paper we report on the preparation of new Al\textsubscript{2}O\textsubscript{3}/CeO\textsubscript{2} and Al\textsubscript{2}O\textsubscript{3}/La\textsubscript{2}O\textsubscript{3}-supported Pt nanoparticles and on their use as efficient catalytic systems for the H\textsubscript{2} production via glycerol SR. We have demonstrated how reducing the support acidity by means of basic additives such as CeO\textsubscript{2} and La\textsubscript{2}O\textsubscript{3}, significantly improves the catalyst stability and selectivity reducing, at the same time, the formation of undesirable products and coke depositions.

A complete characterization of the new catalytic systems together with the study of their stability and selectivity in the glycerol SR process are also provided with the aim of rationalizing the effective role of the support composition on the catalytic performance of the Pt nanoparticles.

Results and Discussion

Catalytic activity

Running-up experiments under SR conditions has shown a strong influence of the composition of the catalyst support on the conversion of glycerol into syn-gas. Fig. 1 shows the conversion of glycerol to gaseous products, calculated on the basis of the
flow of the gas at the outlet of the reactor (after condensation of the non-volatile compounds), as a function of the catalytic temperature, while Fig. 2 illustrates the composition of the gas phase produced throughout the catalytic process as revealed by GC analysis.

A typical Pt/Al₂O₃ catalyst exhibits a poor activity in the glycerol SR at low temperature with a minimum in the glycerol conversion to syn-gas in the range of 350 – 400 °C. At the same time, very low gas flows are generally recorded (~ 25 mL min⁻¹) and significant amounts of hydrocarbons (CH₄, C₂H₆ and C₃H₈) are detected in the effluents. Finally, the collected liquid fraction presents a typical yellow – brownish colour, suggesting the formation of heavy oxygenated hydrocarbons produced by condensation side-reactions. A qualitative GC-MS analysis of the liquid fractions collected during the reaction at 350 – 400 °C confirmed the presence of high quantities of un-reacted glycerol and the presence of a large number of by-products. The most abundant are hydroxyacetone, 1,2-propanediol, ethylene glycol and their monoesters with acetic acid. The presence of acrolein or acrilic acid cannot be excluded, since the clear attribution of all the peaks revealed in the chromatogram is not possible, due to the large number of by-products present almost in traces. Other authors have observed a similar low activity for catalytic Pt nanoparticles over carbon supports. This effect has been ultimately attributed to a rapid carbon monoxide passivation of the catalyst active sites already at low temperature. The metal sites passivation by CO favors glycerol dehydrogenation at the acidic sites of the support, ultimately increasing the amount of undesired by-products. A strong increase in the glycerol conversion to syn-gas is observed on the same catalyst by increasing the reaction temperature, although the complete conversion is never reached. H₂ and CO₂ are produced above 450 °C with the presence of a small amount of CH₄ and traces of CO (over 550 °C).

The poor activity of the Pt/Al₂O₃ catalyst in the glycerol SR can be ascribed to the occurrence of a complex network of side – reactions, including dehydration / condensation / polymerization reactions, promoted by the acid sites of the support, as well as dehydrogenation / hydrogenation reactions promoted by the Pt nanoparticles. Comparable results have been recently reported for the SR of glycerol using Al₂O₃ – supported Ni catalysts as well as for aqueous-phase reforming over Al₂O₃ – supported Pt catalysts.

Notably, Pt/Al₂O₃ catalysts doped with either CeO₂ or La₂O₃ exhibit different catalytic activities and selectivity. Although a trend similar to that recorded for Pt/Al₂O₃ is observed for temperature lower than 300 °C, a sharp increase is reached for the doped systems between 350 – 400 °C, leading to glycerol conversions close to the maximum (Fig. 1). While temperatures up to 300 °C generate H₂ and CO (suggesting the glycerol decomposition as the main operative process – Eq. 2), over 350 °C a significant increase in H₂ and CO₂ production is observed, which indicates that the WGS equilibrium is also operative (Fig. 2). CH₄ is the major by-product observed while only traces of C₂H₆ and C₂H₄ are present.

A decrease in the gas flow in finally observed for temperatures over 400 °C. A similar effect of La₂O₃ and CeO₂ has been already reported by Iriondo et al. studying the effect of various doping agents on the activity of Ni/Al₂O₃ catalyst in the glycerol SR and APR. While Pt/CeO₂/Al₂O₃ shows a decrement up to 500 °C, where the glycerol conversion stabilizes around 50%, the Pt/La₂O₃/Al₂O₃ system is characterized by a second maximum around 550 °C, which affects only marginally the final gas stream composition. For both the doped catalysts, only a slight increase in the CO concentration is observed at high temperature, which is reasonably attributed to the WGS exothermic equilibrium. The gas stream profile for Pt/La₂O₃/Al₂O₃ (two relative maxima in the glycerol conversion) is perfectly reproducible and it is maintained for different batches of fresh catalyst. Such a profile is probably associated to a progressive deactivation / reactivation of the
Table 1. Molar ratios of the main gaseous products during glycerol steam reforming experiments.\(^{[25]}\)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature (°C)</th>
<th>H(_2)/CO</th>
<th>H(_2)/CO(_2)</th>
<th>CO/CO(_2)</th>
<th>CH(_4)/H(_2)</th>
</tr>
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<tbody>
<tr>
<td>Pt/Al(_2)O(_3)</td>
<td>250</td>
<td>1.12</td>
<td>36.20</td>
<td>32.37</td>
<td>0.171</td>
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<tr>
<td></td>
<td>300</td>
<td>0.95</td>
<td>20.18</td>
<td>21.23</td>
<td>0.217</td>
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<tr>
<td></td>
<td>350</td>
<td>1.35</td>
<td>1.56</td>
<td>1.16</td>
<td>0.262</td>
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<tr>
<td></td>
<td>400</td>
<td>1.31</td>
<td>2.49</td>
<td>1.91</td>
<td>0.105</td>
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<tr>
<td></td>
<td>450</td>
<td>4.42</td>
<td>1.94</td>
<td>0.44</td>
<td>0.137</td>
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<tr>
<td></td>
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<td>0.134</td>
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<td></td>
<td>550</td>
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<td>2.27</td>
<td>0.31</td>
<td>0.054</td>
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<td></td>
<td>600</td>
<td>6.43</td>
<td>2.37</td>
<td>0.37</td>
<td>0.044</td>
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<td>10.28</td>
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<td>0.06</td>
<td>0.066</td>
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<td>1.65</td>
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<tr>
<td></td>
<td>550</td>
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<td>2.06</td>
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<tr>
<td></td>
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<tr>
<td>Pt/CeO(_2)/Al(_2)O(_3)</td>
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<td>1.78</td>
<td>4.97</td>
<td>2.79</td>
<td>0.090</td>
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<tr>
<td></td>
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<td>4.15</td>
<td>2.26</td>
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</tr>
<tr>
<td></td>
<td>350</td>
<td>26.79</td>
<td>2.01</td>
<td>0.07</td>
<td>0.054</td>
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<tr>
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<td>2.01</td>
<td>0.09</td>
<td>0.054</td>
</tr>
<tr>
<td></td>
<td>450</td>
<td>21.14</td>
<td>1.82</td>
<td>0.09</td>
<td>0.094</td>
</tr>
<tr>
<td></td>
<td>500</td>
<td>13.58</td>
<td>1.86</td>
<td>0.14</td>
<td>0.094</td>
</tr>
<tr>
<td></td>
<td>550</td>
<td>15.75</td>
<td>1.91</td>
<td>0.12</td>
<td>0.083</td>
</tr>
<tr>
<td></td>
<td>600</td>
<td>12.62</td>
<td>2.13</td>
<td>0.17</td>
<td>0.024</td>
</tr>
</tbody>
</table>

[a] Condition: 1.00 g catalyst, 0.32 mL min\(^{-1}\) of C\(_2\)H\(_8\)O\(_2\) (30 wt%) water solution.

catalytic sites with the catalyst temperature with no apparent modification of the catalyst selectivity. Accordingly, detectable amounts of un-reacted glycerol and by-products are invariably identified by GC-MS analysis of the liquid fractions collected from the reactor working at temperature higher than 450 °C with doped Pt/Al\(_2\)O\(_3\) catalysts.

Table 1 presents the evolution of relative ratios between the main products for the various catalysts at different temperatures. For Pt/Al\(_2\)O\(_3\), the highest CH\(_4\)/H\(_2\) is observed, confirming that this catalyst presents the highest selectivity to the hydrocarbon production. For Pt/La\(_2\)O\(_3\)/Al\(_2\)O\(_3\), the analysis of the molar ratios confirms that below 300 °C the glycerol decomposition (Eq. 2) is operative (H\(_2\)/CO ratio close to the theoretical value of 1.33) while, increasing the temperature, the WGS in also involved approaching the complete steam reforming process (Eq. 1) with a H\(_2\)/CO \sim 2.33. At the same time, the CO/CO\(_2\) ratio is strongly reduced increasing the catalyst temperature. Finally, for Pt/CeO\(_2\)/Al\(_2\)O\(_3\), the occurrence of the WGS reaction also at low temperature is confirmed by H\(_2\)/CO \sim 1.33 already at 250 °C.

The preservation of the catalyst stability throughout a catalytic process represents one of the most important goals to be addressed while designing new catalytic systems. To assess the practical use of our Pt-based catalysts, long term stability test were performed. The catalyst stability for the doped samples has been studied in the glycerol SR process at 350 °C (Fig. 3), where the plain Pt/Al\(_2\)O\(_3\) catalyst shows its lowest catalytic performance. Both doped catalysts present a good stability for at least 20 h. While the Pt/CeO\(_2\)/Al\(_2\)O\(_3\) system exhibits a very fast decrease in the glycerol conversion to syn-gas after 20 h, the La\(_2\)O\(_3\)-doped catalyst maintain a high stability over a period of 50 h. Notably, the selectivity in the different products remain almost constant throughout the catalyst reaction.

The sharp decrease observed for the Pt/CeO\(_2\)/Al\(_2\)O\(_3\) was also previously reportd in the case of Pt/Al\(_2\)O\(_3\).\(^{[25]}\) The process was interpreted on the bases of the fact that the reactor initially operates at 100% conversion and glycerol is present only in the upstream portion of the catalyst bed in the tubular reactor. Therefore, the deactivation front moves from the reactor inlet to the outlet as olefinic species are formed from glycerol on the Al\(_2\)O\(_3\) acid sites, followed by deposition of coke from these species covering the Pt surface sites.\(^{[25]}\)

![Figure 3. Stability test over doped Pt/Al\(_2\)O\(_3\) catalyst. Upper part: Percentage glycerol conversion to gas phase products. Lower part: Gas phase composition using Pt/La\(_2\)O\(_3\)/Al\(_2\)O\(_3\) (a) and Pt/CeO\(_2\)/Al\(_2\)O\(_3\) (b). Condition: 1.00 g catalyst, 0.32 mL min\(^{-1}\) of C\(_2\)H\(_8\)O\(_2\) (30 wt%) water solution, T = 350 °C.](image-url)

Despite the relatively high ceria loading (20wt%), the catalyst surface still presents a significant amount of acidic sites (see NH\(_3\)-TPD below). This might be due to the fact that the calcination at 700 °C leads to a partial agglomeration of the ceria into relatively small but appreciable nanoparticles. Indeed, assuming for simplicity the formation of ceria particles with cube shape with an edge of \(\sim 4.3\) nm (see XRD section below), the resulting ceria surface area would be around \(7 \text{ m}^2 \text{ g}^{-1}\), which correspond to less...
Table 2. Physisorption and chemisorption results on the fresh catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA [a] (m² g⁻¹)</th>
<th>dₚ [b] (nm)</th>
<th>CPV [c] (mL g⁻¹)</th>
<th>H/Pt [d]</th>
<th>PS [e] (nm)</th>
<th>CS [f] (nm)</th>
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<tbody>
<tr>
<td>Al₂O₃</td>
<td>97</td>
<td>11</td>
<td>0.367</td>
<td>---</td>
<td>---</td>
<td>---</td>
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<tr>
<td>Pt/Al₂O₃</td>
<td>96</td>
<td>11</td>
<td>0.349</td>
<td>0.75</td>
<td>1.4</td>
<td>1.5</td>
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<tr>
<td>La₂O₃/Al₂O₃</td>
<td>91</td>
<td>12</td>
<td>0.338</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Pt/La₂O₃/Al₂O₃</td>
<td>89</td>
<td>11</td>
<td>0.323</td>
<td>0.68</td>
<td>1.6</td>
<td>1.5</td>
</tr>
<tr>
<td>CeO₂/Al₂O₃</td>
<td>100</td>
<td>11</td>
<td>0.292</td>
<td>---</td>
<td>---</td>
<td>---</td>
</tr>
<tr>
<td>Pt/CeO₂/Al₂O₃</td>
<td>96</td>
<td>11</td>
<td>0.281</td>
<td>0.48</td>
<td>2.3</td>
<td>nd [g]</td>
</tr>
</tbody>
</table>

[a] Specific Surface Area from the BET analysis; [b] Maximum of the BJH pore distribution calculated on the desorption branch; [c] Cumulative Pore Volume; [d] H/Pt rate obtained from H₂ chemisorption assuming a spherical geometry; [e] Average Pt Particle Size obtained from H₂ chemisorption assuming a spherical geometry; [f] Average Pt Crystallite Size determined by XRD technique; [g] After reduction at 500 °C, the sample was oxidized at 427 °C flowing O₂ (5%) / Ar (30 mL min⁻¹), then reduced at 100 °C flowing H₂ (5%) / Ar (30 mL min⁻¹) and finally evacuated at 400 °C for 4h, according to Ref. [59, 64]. Not determined.

Characterization of fresh catalysts

Temperature Programmed Reduction (TPR) profiles of the investigated samples are presented in Fig. S1 (see Supporting Information). All samples containing Pt are featured by a broad reduction process with a maximum around 120 °C, related to the reduction of PtOₓ species formed during the calcination treatment. While Pt/CeO₂/Al₂O₃ shows an important H₂ consumption over 500 °C due to the bulk reduction of CeO₂ the Pt/Al₂O₃ and Pt/La₂O₃/Al₂O₃ samples do not show any reduction process over 400 °C.

Different types of PtOₓ species can be obtained from the oxidation of the Pt/Al₂O₃ catalyst from oxygen passivated Pt particles (when the oxidation is performed at room temperature) to the formation of PtAl₂O₅ species (by heating Pt nanoparticles in the presence of Al₂O₃ over 600 °C). In our systems, the calcination step at 500 °C is expected to generate basically PtO₂ although the high nanoparticle dispersions do not allow for a definitive structural confirmation of the Pt-species (see XRD section). The PtO₂ reduction should occur almost quantitatively under a stream of H₂ between 100 and 300 °C, depending on the metal loading, the nature of the support and the metal dispersion.

Such a result indicates that the catalyst activation protocol does not affect the structural characteristics of the doping agent.

The XRD characterization of the supported Pt nanoparticles is generally a difficult task when complex pattern of the support are combined with a low and broadened pattern of the metal phase. In any case, an accurate study can be done by comparing the patterns of the support and of the catalyst within a Rietveld procedure.

In order to separate the platinum scattering from the scattering of the support, the air corrected diffraction pattern of the catalysts was fitted by the Rietveld methods using platinum fcc structure and the experimental diffraction pattern of the support. This analytical method allows also the quantitative evaluation of the metal phase. In this way, a further internal
validity test of the line broadening analysis results \[67\] (see Supporting Information, Figs. S2 – S4). The main Pt crystallite sizes are listed in Table 2. Pt crystallite sizes of 1.5 ± 0.2 nm has been calculated for both Pt/Al\(_2\)O\(_3\) and Pt/La\(_2\)O\(_3\)/Al\(_2\)O\(_3\), with a good agreement with the H\(_2\) chemisorption experiments. In the case Pt/CeO\(_2\)/Al\(_2\)O\(_3\) the low quality of separation of XRD pattern of the metallic phase from the CeO\(_2\)/Al\(_2\)O\(_3\) support does not allow for an accurate determination of the Pt nanoparticle distribution (Fig. S4). Moreover, the Rietveld refinement of the XRD pattern for the reduced Pt/CeO\(_2\)/Al\(_2\)O\(_3\) species accounts for a ~ 5.5 wt% of Pt loading, which is almost the double of the nominal Pt amount. This is a further test of the low quality of the evaluation of the XRD pattern of platinum. In contrast, Pt contents of 2.7 wt% and 2.3 wt% have been obtained for the Pt/Al\(_2\)O\(_3\) and Pt/La\(_2\)O\(_3\)/Al\(_2\)O\(_3\), respectively, which well fits with the nominal Pt loading. The low quality of the XRD spectra of the active phase of Pt/CeO\(_2\)/Al\(_2\)O\(_3\) could be attributed to high scattering factors of CeO\(_2\), the reflections of which dominate the XRD pattern. Finally, the lack of clear reflections attributable to metallic Pt in all samples suggests a very high dispersion of Pt nanoparticles (dimension < 1 nm) on the surface of the catalyst, in agreement with the H\(_2\) chemisorption results.

The acidity of the different catalysts were determined by NH\(_3\)-TPD. NH\(_3\) desorption from Al\(_2\)O\(_3\)-based materials is usually reported in the range between 100 – 500 °C for NH\(_3\) adsorbed on the Brønsted acid sites (OH groups)\[^{[69]}\].

As Fig. 5 shows, the influence of La\(_2\)O\(_3\) or CeO\(_2\) doping results in a strong effect on the population of acidic sites and consequently on the amount of adsorbed NH\(_3\). Pt/Al\(_2\)O\(_3\) presents the highest amount of NH\(_3\) adsorbed on the surface of the catalyst. At least two superimposed desorption peaks can be identified (~ 220 and ~ 325 °C), related to weak and medium/strong adsorbed NH\(_3\). The introduction of La\(_2\)O\(_3\) and CeO\(_2\) results in a great reduction of the amount of desorbed NH\(_3\) together with a significant shift to lower temperature for both the desorption maxima. Since comparable surface areas were measured for all the samples, these results indicate that the addition of basic promoters reduce the number and the strength of the acidic sites present on the surface of the catalysts. The significantly lower acidity of the La\(_2\)O\(_3\)-based system can be associated with the very high dispersion of the doping oxide on the alumina surface.

The reduced acidity of the materials promoted by the La\(_2\)O\(_3\) and CeO\(_2\) doping justify the better performances of these catalysts in the glycerol SR. The worst reforming activity observed with Pt/Al\(_2\)O\(_3\) is therefore ascribed to the occurrence of the undesired side-reaction of dehydration / condensation catalyzed by the acid sites of the support.

### Table 3. Physisorption and chemisorption results on the aged catalysts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>SSA (^{[a]}) (m(^2) g(^{-1}))</th>
<th>d(_0) (^{[b]}) (nm)</th>
<th>CPV (^{[c]}) (mL g(^{-1}))</th>
<th>H/Pt (^{[d]})</th>
<th>PS (^{[e]}) (nm)</th>
<th>CS (^{[f]}) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Pt/Al(_2)O(_3)</td>
<td>78</td>
<td>15</td>
<td>0.268</td>
<td>0.35</td>
<td>3.2</td>
<td>3.0</td>
</tr>
<tr>
<td>Pt/Al(_2)O(_3)/Al(_2)O(_3) run-up at 600 °C</td>
<td>69</td>
<td>17</td>
<td>0.161</td>
<td>0.32</td>
<td>3.6</td>
<td>2.7</td>
</tr>
<tr>
<td>Pt/La(_2)O(_3)/Al(_2)O(_3) Stability at 350 °C</td>
<td>80</td>
<td>16</td>
<td>0.270</td>
<td>0.21</td>
<td>5.3</td>
<td>2.2</td>
</tr>
<tr>
<td>Pt/CeO(_2)/Al(_2)O(_3) run-up at 600 °C</td>
<td>78</td>
<td>15</td>
<td>0.234</td>
<td>0.42</td>
<td>2.7</td>
<td>nd [^{[g]}]</td>
</tr>
<tr>
<td>Pt/CeO(_2)/Al(_2)O(_3) Stability at 350 °C</td>
<td>95</td>
<td>16</td>
<td>0.276</td>
<td>0.48</td>
<td>2.4</td>
<td>nd [^{[g]}]</td>
</tr>
</tbody>
</table>

\[^{[a]}\] Specific Surface Area from the BET analysis; \[^{[b]}\] Maximum of the BJH pore distribution calculated on the desorption branch; \[^{[c]}\] Cumulative Pore Volume; \[^{[d]}\] H/Pt ratio obtained from H\(_2\) chemisorption at -94 °C of the samples previously reduced at 500 °C for 5h; \[^{[e]}\] Average Pt Particle Size obtained from H\(_2\) chemisorption assuming a spherical geometry; \[^{[f]}\] Average Pt Crystal Size determined by powder XRd; \[^{[g]}\] Not determined.

**Effect of CeO\(_2\) and La\(_2\)O\(_3\) doping on the catalysts’ stability and origin of the catalyst deactivation effects**

Exhaust catalysts, as obtained after aging under glycerol SR conditions, have been fully characterized in an attempt of highlighting eventual structural catalyst modifications as well as deactivation phenomena occurring during the catalytic process. Table 3 summarizes the physi- and chemisorption results of the aged samples. A significant reduction of the accessible Pt active sites is clearly evident. This effect could be due to the concomitant occurrence of several processes:

- partial sintering of the Pt nanoparticles
- deposition of carbonaceous residues onto the Pt active sites (coke)
- progressive occlusion of the pores onto the catalyst support

The latter point is confirmed by the N\(_2\) physisorption experiments where a progressive decrease of the specific surface areas and pore volumes is recorded for all aged samples. Calculation of the Pt nanoparticle sizes from the XRD patterns (Fig. 6) of the aged catalysts (after subtracting the contribution of the support) has shown an appreciable increase in the Pt nanoparticle dimensions for both Pt/Al\(_2\)O\(_3\) and Pt/La\(_2\)O\(_3\)/Al\(_2\)O\(_3\) (see Supporting Information Figs. S5 and S6). This result well fits with the H\(_2\) chemisorption experiments. The reduction of the H/Pt values can be actually explained by the occurrence of the following effects:

- sintering of the Pt nanoparticles
- active sites passivation due to formation of coke deposits.

![Figure 5: NH\(_3\)-TPD profiles recorded for the samples reduced at 500 °C: Pt/Al\(_2\)O\(_3\) (a), Pt/La\(_2\)O\(_3\)/Al\(_2\)O\(_3\) (b) and Pt/CeO\(_2\)/Al\(_2\)O\(_3\) (c).](image-url)
has finally provides a clear identification of the decomposition products (basically H2O and CO2). The TGA profiles and the curves related to CO2 evolution are reported in Fig. 7. From a perusal of Table 2, Table 3 and Fig. 7, it is possible to conclude that both processes, metal sintering and coke deposition, are operative in all catalytic tests.

H2O evolution due to the humidity adsorbed at the catalyst surface (unreported data) with no concomitant CO2 formation, and responsible for the initial catalyst weight loss, is observed below 200 °C for all the analyzed samples. Above 200 °C, carbonaceous deposits start to burn, with the production of only marginal amounts of H2O. As Fig. 7 shows, after running up experiments, Pt/Al2O3 exhibits the highest weight loss (6.4wt%), with a significant CO2 evolution between 250 and 600 °C. This observation is perfectly in line with its lower catalytic activity. A high amount of carbonaceous compounds actually covers the catalyst surface during the reforming process, as a consequence of the higher acidity of the catalyst support. On the contrary, Pt/La2O3/Al2O3 and Pt/CeO2/Al2O3 show a significantly lower amount of adsorbed organic residues (4.1wt% and 1.9wt%, respectively).

The reduced amount of carbonaceous deposits could be ultimately related to the lower acidity of the catalyst supports.[25,69] Similar CO2 evolution profiles and comparable temperature ranges for Pt/La2O3/Al2O3 and Pt/Al2O3 suggest a similar nature of the carbonaceous deposits. In contrast, the Pt/CeO2/Al2O3 sample shows a symmetric CO2 evolution peak in a lower temperature range. This result can be reasonably ascribed to either a less graphitic nature of the coke deposits and/or to a cooperative effect of CeO2 in the combustion of the carbonaceous materials. In fact, it is well known that the introduction of CeO2-based additives to a reforming catalyst can prevent the deposition of coke-based materials or favor their elimination during oxidative treatments.[35,39]

Prolonged reactivity tests at 350 °C with both Pt/La2O3/Al2O3 and Pt/CeO2/Al2O3 reveal the formation of a low amount of carbonaceous deposits thus suggesting that the higher the catalyst temperature the higher the amount of the coke deposits. For the Pt/La2O3/Al2O3 catalyst, the lower reaction temperature reduces the polymerization reaction (weight loss 3.3wt%), leading to carbonaceous deposits which are easily removed during TGA (Fig. 7d). Finally, despite the deep and sudden loss of reforming activity, very low amount of carbonaceous deposits were removed during the TGA analysis (~0.5% of weight loss) around 600 – 700 °C (Fig. 7e).

Fig. 8 shows representative HR-TEM images acquired for the spent Pt/La2O3/Al2O3 after stability test under glycerol SR conditions at 350 °C for 52h. Pt nanoparticles can be easily recognized in the images as dark particles and by the spacing between the lattice planes. The dimensions of the Pt nanoparticles are in the range of 2 – 3 nm, in good agreement with XRD and the size of the nanoparticles is only marginal affected by the prolonged use under glycerol stem reforming (as evidenced by XRD and HR-TEM).

The Thermo Gravimetric Analysis (TGA) conducted on the exhaust catalysts has allowed for the assessment of both the amount and the type of carbonaceous compounds deposited onto the catalyst surface during the reaction process. Coupling the TGA with a quadrupole for the MS gas analysis of the volatiles
EDX analysis confirmed the presence of lanthanum although no clear attribution to a particular phase is possible (as revealed also by XRD). The Al₂O₃ support appears in the HR-TEM images as welldefined crystallites with dimensions of 15–20 nm. Some examples of relatively clean particles of the support are present in the upper part of Fig. 8, where the lattice plane of δ-Al₂O₃ can be observed.

Some carbonaceous amorphous regions of few nanometers have been observed on the surface of the used catalyst. However, suitable information about the spatial distribution of carbon species on the active particles cannot be unambiguously determined. Despite this, the reduction of the H/Pt ratio measured by H₂ chemisorption suggests that the amorphous carbon deposits partially cover the Pt nanoparticles, since the real dimension of the nanoparticles is only marginally affected by their prolonged use under glycerol SR (as evidenced by XRD and HR-TEM).

Conclusions

The present study deals with the effects deriving from the addition of basic oxides (La₂O₃ and CeO₂) to Pt/Al₂O₃ catalysts for the H₂ production by glycerol Steam Reforming. The most relevant conclusions of this work can be summarized as follow:

1. Pt/Al₂O₃ catalyst promotes the H₂ production only at high temperature (>500°C), which is ascribed to the occurrence of side reactions promoted by the acidic sites on the Al₂O₃ support. A lot of undesired by-products formed by dehydration/polymerization reactions were detected in the liquid effluent from the reactor.

2. La₂O₃ and CeO₂ deposited onto Al₂O₃ improve the catalytic performances of the Pt nanoparticles, decreasing the acidity of the support, as evidenced by NH₃-TPD. Such a metal oxide doping allows glycerol to be completely converted into syn-gas already at 350°C efficiently promoting, at the same time, the Water-Gas Shift reaction. Finally, little amounts of CH₄ are produced as a result of concomitant hydrogenation reactions.

3. The addition of La₂O₃ and CeO₂ significantly improves the catalyst stability as a consequence of the reduced acidity of the Al₂O₃ support. Moreover, the amount of carbon deposits is significantly reduced as compared to the plain Pt/Al₂O₃ sample.

Despite these positive effects, the CeO₂-doped catalyst deactivates quickly after 20 hours at 350°C while a higher stability is shown by the La₂O₃-doped sample (over 50 h).

4. The detailed characterization of the fresh and spent catalysts allows to better understand the behavior or our doped catalysts under glycerol SR conditions. The slight deactivation observed for Pt/La₂O₃/Al₂O₃ catalyst could be related essentially to coke deposition on the catalyst surface, resulting in a significant Pt coverage (as assessed by H₂ chemisorption and HR-TEM). The effect of Pt sintering (XRD and HR-TEM) or surface area decrease is only marginal.

Experimental Section

Catalysts preparation

All studied catalysts have been supported on Al₂O₃ beads to reduce the overpressure inside the reactor during activity tests. Al₂O₃ (Puralox TH100) beads have been kindly provided by SASOL in the form of spheres (diameter ~1.0mm) and have been calcined at 900°C for 24h before their use in order to remove all organic binders and stabilize their texture.

The beads were modified by introducing either La₂O₃ or CeO₂ in order to reduce the catalyst support acidity and evaluate (in the case of CeO₂) the effects of the presence of a redox active component. La₂O₃ (5 wt%) was introduced by impregnation of the Al₂O₃ spheres using a solution of La(NO₃)₃•9H₂O in water. Afterwards, the solvent was removed by evaporation at reduced pressure and the resulting material was dried at 120°C overnight and calcined in static air at 700°C for 5h, respectively. CeO₂ (20 wt%) was introduced by impregnation of the Al₂O₃ spheres (previously degassed at 225°C overnight) using an isooctane solution of Ce(OC₃H₇)₃. The latter was prepared according to literature procedures. After soaking of the Al₂O₃ spheres, the solvent was removed by evaporation at reduced pressure and the resulting material was dried at 120°C overnight and calcined in static air at 700°C for 5h, respectively. The amounts of La₂O₃ and CeO₂ were optimized in order to introduce the maximum quantity of the dopant oxide without any significant variations of the support surface area (see Table 2).

Pt (in the amount of 3wt%) was loaded on the bare or modified Al₂O₃ spheres by impregnation using a water solution of Pt(NO₃)₄. After drying at 120°C overnight, the products were calcined at 500°C for 5h.

Catalytic activity

In a typical procedure 1 g of the fresh catalyst was loaded over fused SiO₂ granules (-4+16mesh; Sigma-Aldrich), in the middle of a ¼-inch outer diameter stainless-steel reactor placed in an electrical furnace. Fused SiO₂ granules were then used to cover the catalytic bed to favor the vaporization of the liquid reagents injected from the top of the reactor. Type-K thermocouple was finally attached to the outside of the reactor to measure the reactor temperature. Fresh catalysts were reduced before each catalytic test by treatment with pure H₂ (25 mL min⁻¹) at 500°C for 5h. After purging the reactor with Ar and cooling to the desired temperature, a water solution of glycerol (30wt%) was introduced at its top by means of a KNF pump (Model STEPDOS 03 RC) which allows for a constant flow rate of 0.32 mL/min throughout the catalytic process. The outlet effluents were cooled through a water-condenser to remove all liquid fractions. Volatiles were analyzed on-line by GC using a Hewlett Packard 6890 gas chromatograph and then vented. A Molisieve 5A column, using Ar as carrier, connected to a thermal conductivity detector (TCD) was used to follow the H₂, O₂, N₂, CH₄ and CO production. A PoraPLOT Q column, using He as carrier, connected to both a methanator and a
flame ionisation detector (FID) was used to analyze all carbon-containing compounds.

After reducing all catalysts at 500 °C, the systems are cooled to 250°C and the liquid injection starts. The catalyst temperature is maintained at 250 °C for 1h before starting the GC analysis. Afterwards, the catalyst temperature is increased step-by-step up to 600°C (step 50 °C), and volatiles produced at the reactor outlet are systematically analyzed throughout the whole temperature range. For stability tests, after the reduction step, the systems are cooled to the final temperature (350°C), at which stage the injection of the glycerol solution and the GC analysis of volatiles produced at the reactor outlet, start.

Catalysts characterization

All catalysts were fully characterized with respect to their morphological and structural properties both as freshly prepared systems and aged catalysts (run-up test up to 600°C and stability test at 350°C).

H2 chemisorption and physisorption measurements were conducted using a Micromeritics ASAP 2020 analyzer. N2 physisorption isotherms were collected at -196°C on 0.1 g of sample, after evacuation at 350 °C overnight. Surface area and pore distribution were obtained applying the BET and BJH models, respectively. H2 chemisorption experiments are conducted at -94 °C (solid/liquid acetone bath) on 0.2 g of catalyst. The calcined samples were pre-reduced in a flow of H2 (35 mL min⁻¹) at a heating rate of 10 °C min⁻¹ up to 500°C (standard activation temperature). After 5 h at this temperature, the samples were evacuated at 400 °C for 4 h, and cooled under vacuum to the adsorption temperature (-90 °C). Typically, an equilibration time of 10 min was employed. Adsorbed volumes were determined by extrapolation to zero pressure of the linear part of the adsorption isotherm (100 - 400 torr) after elimination of reversible hydrogen adsorption. A chemisorption stoichiometry H : Pt = 1:1 was assumed. Aged samples were not subjected to standard cleaning procedure to avoid metal re-dispersion and/or carbonaceous species removal. These samples were pre-reduced for 1 h in a flow of H2 (5%) / Ar (35 mL min⁻¹) at a heating rate of 10 °C/min up to 100 °C, evacuated at 400 °C for 4 h and subjected to chemisorption measurement at -90 °C.

A Philips X’Pert vertical goniometer with Bragg-Brentano geometry, connected to a highly stabilized generator, was used for the XRD measurements. A focusing graphite monochromator and a proportional counter with a pulse-height discriminator were used. Nickel-filtered Cu Kα radiation and a step-by-step technique are employed (steps of 28 = 0.05°), with collection times of 10 s step⁻¹. Line broadening analysis (LBA) was carried out using a previously published method [3]. The quantitative phase analysis by X-ray diffraction was performed using the Rietveld method (DBWS9600 computer program written by Sakhvil & Young and modified by Rielo et al.[2]).

Temperature Programmed Reductions (TPR) were performed on 0.1 g of the calcined materials. The samples were pre-treated at 500 °C for 1 h by pulsing 100 µL of O2 in an Ar flow every 75 s, then purged with Ar at 150 °C for 15 min and cooled to RT. H2 (5%) / Ar was admitted into the reactor and the flow allowed to stabilize for 30 min before increasing the temperature to 1000 °C at 10 °C min⁻¹. After TPR, the samples were outgassed under an Ar flow at 1000 °C for 15 min and cooled to 427 °C, at which temperature oxidation was carried out with pulses of O2 in an Ar flow for 1hour. H2 consumption was monitored using a TCD.

Temperature-programmed desorption (TPD) of ammonia was conducted in a home-made flow apparatus using a mass spectrometer Hiden HPR20 as analyzer. In a typical NH3-TPD experiment, about 0.25 g of the sample was loaded in U-shaped quartz microreactor. The samples were reduced flowing H2 (25 mL min⁻¹) at 500 °C for 5h. After the treatment, the adsorbed H2 was removed by flowing the system with Ar at 500 °C for 30 min. Afterwards, the samples were cooled at 110 °C under the inert gas flow. For NH3 adsorption, the reduced samples were saturated flowing NH3 (10%) / Ar (50 mL min⁻¹) at 110 °C for 30 min. After NH3 adsorption, the sample was flushed in Ar flow at 110 °C for 1h to remove physically adsorbed NH3. The NH3-TPD profile for each sample was recorded by increasing the temperature from 110 to 800 °C with a heating rate of 10 °C min⁻¹ under flow of Ar (50 mL min⁻¹). The desorbed products were analyzed by means of a mass spectrometer operating in the electron impact mode with a ionization energy of 35 eV. The desorbed species were identified on the basis of the intensity of various mass fragments. In particular, the peak m/z = 16 was used to follow the evolution of ammonia because the parent peak (m/z = 17) was influenced by the desorbed water.

The carbon deposits on the aged catalysts were characterized using Thermo-Gravimetric Analysis (TGA). TGA analysis were performed using a EXSTAR Thermo Gravimetric Analyzer (TG/DTA) Seiko 6200 coupled with a mass spectrometer ThermoStar™ GSD 301 T for the analysis of the exhaust gases. Typically, 20 mg of the aged samples were loaded in the instrument and the TGA was performed in flowing air (flow rate 100 mL.min⁻¹) with a heating rate of 10 °C min⁻¹.

High Resolution Transmission Electron Microscopy (HR-TEM) images were collected on representative samples with a Jeol 3010 high resolution electron microscope (1.7 nm point-to-point) operating at 300 keV using a Gatan slow-scan CCD camera (mod.794). The samples were suspended in hexane and a single drop was placed on a 200-mesh copper carbon-hole grid. Images were collected with a magnification of ~ 600000x.

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Keywords: reforming of glycerol; heterogeneous catalyst design; gas phase reforming; Platinum based catalyst; lanthanum oxide; cerium oxide


Entry for the Table of Contents (Please choose one layout)

Layout 1:

FULL PAPER

Hydrogen is efficiently produced by reforming of glycerol using modified Pt/Al₂O₃ catalysts. The addition of La₂O₃ or CeO₂ strongly promotes the reforming of glycerol, involving also the Water Gas Shift Reaction in the process. The stability performances of Pt/La₂O₃/Al₂O₃ are promising, presenting lower Pt sinterization and coke deposition with respect to Pt/Al₂O₃.

Tiziano Montini, Rakesh Singh, Piyali Das, Barbara Lorenzut, Nicolás Bertero, Pietro Rielo, Alvise Benedetti, Giuliano Giambastiani, Claudio Blanchini, Sergey Zinoviev, Stanislav Miertus and Paolo Fornasiero*

Renewable H₂ from glycerol steam reforming: effect of La₂O₃ and CeO₂ addition to Pt/Al₂O₃ catalysts.
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Tiziano Montini, Rakesh Singh, Piyali Das, Barbara Lorenzut, Nicolás Bertero, Pietro Riello, Alvise Benedetti, Giuliano Giambastiani, Claudio Bianchini, Sergey Zinoviev, Stanislav Miertus and Paolo Fornasiero*

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Figure S1: Temperature Programmed Reduction (TPR) profiles for (a) Pt/Al₂O₃, (b) Pt/La₂O₃/Al₂O₃, (c) Pt/CeO₂/Al₂O₃ and (d) CeO₂/Al₂O₃.
Figure S2: (a) XRD patterns of Pt/Al$_2$O$_3$ after reduction at 500 °C for 5h. After subtraction of the signal for the Al$_2$O$_3$ support, the contribution of Pt can be fitted; (b) size distribution for the Pt nanoparticles.

Figure S3: (a) XRD patterns of Pt/La$_2$O$_3$/Al$_2$O$_3$ after reduction at 500 °C for 5h. After subtraction of the signal for the La$_2$O$_3$/Al$_2$O$_3$ support, the contribution of Pt can be fitted; (b) size distribution for the Pt nanoparticles.
Figure S4: XRD patterns of Pt/CeO$_2$/Al$_2$O$_3$ after reduction at 500 °C for 5h. After subtraction of the signal for the CeO$_2$/Al$_2$O$_3$ support, the quality of the contribution of Pt is not enough to allow a good estimation of the Pt particle size distribution.

Figure S5: (a) XRD patterns of Pt/Al$_2$O$_3$ after glycerol steam reforming up to 600 °C. After subtraction of the signal for the Al$_2$O$_3$ support, the contribution of Pt can be fitted; (b) size distribution for the Pt nanoparticles.
Figure S6: (a) XRD patterns of Pt/La$_2$O$_3$/Al$_2$O$_3$ after glycerol steam reforming up to 600 °C. After subtraction of the signal for the La$_2$O$_3$/Al$_2$O$_3$ support, the contribution of Pt can be fitted; (b) size distribution for the Pt nanoparticles.

Figure S7: (a) XRD patterns of Pt/La$_2$O$_3$/Al$_2$O$_3$ after stability test under glycerol steam reforming at 350 °C for 55 h. After subtraction of the signal for the La$_2$O$_3$/Al$_2$O$_3$ support, the contribution of Pt can be fitted; (b) size distribution for the Pt nanoparticles.
Figure S8: (a) XRD patterns of Pt/CeO$_2$/Al$_2$O$_3$ after stability test under glycerol steam reforming at 350 °C for 28 h. No appreciable differences are observed with respect to the XRD patterns of the reduced sample.