ABSTRACT – The effect of the lanthana content on the textural and structural properties of \( \text{Pt/} \text{La}_2\text{O}_3\text{-Al}_2\text{O}_3 \) was studied. All catalysts were prepared by the sol-gel method using appropriate \( \text{Al} \) and \( \text{La} \) precursors. A 1 wt.% of platinum was incorporated to the solids. The catalysts were characterized by XRD, chemical analysis, Raman spectroscopy, \( \text{N}_2 \) adsorption isotherms and TPR. The increased activity observed during the dry reforming of methane was due to the ability of \([\text{LaPtO}_x]\text{Pt}^0\)-like entity to eliminate the coke. The accessibility of the Pt species to methane and carbon dioxide promoted the reaction by increasing the \( \text{La}_2\text{O}_3 \) content.

1. INTRODUCTION

Although research into the dry reforming of methane commenced in the 1920s, it has recently attracted considerable attention, as it would be an environmentally benign alternative to produce hydrogen. Indeed, the political and environmental concerns are driving society to develop sustainable uses of carbon dioxide, a major greenhouse gas. Therefore, the \( \text{CO}_2 \) reforming of methane for hydrogen production is seen as viable option to supplement the other hydrocarbon reforming processes, i.e. the natural gas and petroleum), provided that lesser effects on global climate and technological advancements in hydrogen production can be achieved. The dry reforming of methane process is represented by: conditions, demonstrating that methyl radicals.

\[
\text{CH}_4 + \text{CO}_2 \rightarrow 2\text{CO} + 2\text{H}_2 \quad \Delta H_{298}^\circ = 247 \text{ kJ.mol}^{-1} \quad (1)
\]

The reaction may occur through carbon dioxide competition against hydrogen and subsequently they are converted into carbon monoxide and water by reverse gas shift reaction (Bradford and Vannice, 1999; TAMOŠIŪNAS et al., 2012).

\[
\text{CO}_2 + \text{H}_2 \rightarrow \text{CO} + \text{H}_2\text{O} \quad \Delta H_{298}^\circ = -41.17 \text{ kJ.mol}^{-1} \quad (2)
\]

A number of solid catalysts, including monometallic Pt-containing alumina, zirconia, titania,
magnesia, active carbon and silica oxides have been explored in the reaction. Also, activity of bimetallic Ni-Pt based catalysts metals supported on niobia, zeolites, hydrotalcites, lanthana, ceria and aluminates showed good initial activity for CO₂ reforming of methane but soon exhibited higher carbon monoxide formation as byproduct and rapid deactivation due to sever coke deposition (Pinheiro et al., 2009).

Among the cited catalysts, the alumina carriers exhibited superior performance in the dry reforming reaction and they were proposed as appropriate systems while the significant lack of thermal stability, low surface area (ca. 100-150 m²·g⁻¹) and deactivation of the metals on alumina surface through sintering limited the applications to the reactions performed even at moderate temperatures, e.g. 500-650 °C. In addition to this, the noble metals are recognized to suitable components to dry reforming reaction and Pt was found to be significantly more active and selective than Rh, Pd or Ru for the reaction (Bradford and Vannice, 1999). The main drawback of the use of Pt remains their limited availability and high cost, especially when using large amounts of this metal.

Therefore, Pt-containing alumina seems to be effective catalysts for the dry reforming. In a previous work (Araujo et al, 2008), Pt based alumina catalysts have been evaluated in the steam reforming of methane. Such materials retained all the advantages of the porous solids with defined dimensions, excellent textural properties without the disadvantage of requiring low temperatures to avoid phase transitions. Particularly, the structural properties acquired by the catalysts for the use of La₂O₃, has provided an additional driving force to the utilization of the Pt/La₂O₃-Al₂O₃ catalysts in reforming reactions.

The outstanding properties of the solid resulted in high conversions due to the La role in avoiding sintering and aggregation of Pt particles during the steam reforming reaction (Araujo et al. 2008). Nevertheless, further improvements in the Pt/La₂O₃-Al₂O₃ catalysts require the La addition in order to achieve a better catalytic performance. Thus, in the present investigation, the mesoporous 1%Pt/1La₂O₃-Al₂O₃ catalysts were evaluated in the CO₂ reforming of methane. The effect of the La₂O₃ amounts on the catalytic activity was analyzed in detail to correlate the textural and structural properties of the solids with the catalytic one.

Examination of the catalyst properties can determine the proper feed ratios of methane and carbon dioxide in addition to a better catalyst for optimizing the hydrogen production. To the best our knowledge, it is the first time that these catalysts are evaluated in the CO₂ reforming of methane.

2. EXPERIMENTAL

2.1. Catalyst Synthesis

The solids were prepared the sol–gel method (Rinaldi and Schuchardt, 2005), by using aqueous solutions of La(NO₃)₃·6H₂O (99.9%, Aldrich), aluminum tri-sec-butoxide (Al(O-§Bu)₃, p.a., 99%, Merck), and absolute ethanol (Merck 99.5%). The concentrations of Al³⁺ and La³⁺ in the solutions were varied to change Al/La ratio by keeping a constant cations (Al³⁺ + La³⁺) concentration of x M (0.31, 0.95, 2.0, 4.2 e 7.7 mmol de La III).
In a typical procedure, firstly, 25.6 mL of appropriate lanthanum nitrate solution to obtain \( x \text{La}_2\text{O}_3–\text{Al}_2\text{O}_3 \) xerogels ranging from 1 to 20 wt.% of \( \text{La}_2\text{O}_3 \), was added under stirring to a solution containing 103.5 mmol of aluminum tri-sec-butoxide. 3.25 mol of absolute ethanol was added to the previous mixture by keeping the stirring for 0.5 h. The system was refluxed at 100 °C for 1 h and, then, a 25 mL of a 0.10-mol.L\(^{-1}\) nitric acid solution was added dropwise to the slurry for peptization. The slurry was refluxed for an additional 14 h. Subsequently, the gels obtained were dried for 72 h under air at room temperature. Finally, the resulting xerogels were calcined at 950 °C for 6 h under a flow of synthetic air, yielding a series of \( x \text{La}_2\text{O}_3–\text{Al}_2\text{O}_3 \) mixed oxides.

The solids possessing different lanthana loading amounts were used as carriers for platinum impregnation. Then, the Pt/\( x \text{La}_2\text{O}_3–\text{Al}_2\text{O}_3 \) catalysts were prepared by impregnating a 1 wt.% of Pt using an ethanolic solution of \( \text{H}_2\text{PtCl}_6·6\text{H}_2\text{O} \) (Umicore Brasil). The mixture was stirred for 4 h at room temperature and kept for 1 h at 55 °C. After that the ethanol was removed using a rotary evaporator at 70 °C, the solids were washed, dried and calcined at 350 °C under a flow of synthetic air for 2 h. The catalysts were designed as P1LA, P3LA, P16LA, P12LA, P20LA, where the numbers represents the content of \( \text{La}_2\text{O}_3 \). The letters P, A and L are respectively platinum, aluminum and lanthanum.

### 2.2. Caracterization

X-ray diffraction patterns were recorded using a Rigaku Multiflex diffractometer with a CuK\( \alpha \) radiation operated at 40kV and 40mA The peaks were collected in the 2\( \theta \) of 5°- 80° range with step-sizes of 0.02° and counting times of 2 s.

BET surface area of the samples were measured by using nitrogen as adsorbent at -196 °C. The measurements were carried out on Micromeritics ASAP 2000 equipment.

Temperature-programmed experiments (TPR) were carried out using a Micromeritics Pulse Chemisorb 2705 instrument fitted with a thermo conductivity detector (TCD). The catalysts (ca. 100 mg) were evacuated at 150 °C in a N\(_2\) stream for 1 h. The TPR measurements were performed by heating the samples at a rate of 10 °C.min\(^{-1}\) to 1000 °C under flowing a mixture of 5% H\(_2\)/Ar (50 mL min\(^{-1}\)) while the TCD signal was recorded.

The chemical analyses of Pt, Al and La were performed by inductively coupled plasma-atomic emission spectroscopy (ICP) on PerkinElmer Optima 3300 DV device. Prior to the analyses, 60 mg of sample was digested in a hydrochloric solution.

Raman spectra of the spent catalysts were obtained on the T64000 Raman spectrometer (Jobin Yvon triple spectrometer) under ambient conditions. The wavelength was 514.5 nm.

### 2.3. Catalytic reaction

Catalytic activity testing was performed on dry reforming of methane. At least, 50 mg of the catalysts were placed in a fixed bed stainless reactor inside a vertical furnace. The catalysts were
activated at 650 °C in a flow of hydrogen (50 mL min⁻¹) for 1 h prior to each catalytic run. The reactor was then cooled to the desired reaction temperature (600 °C) under atmospheric pressure in the presence of nitrogen and the reactant mixture (CH₄/CO₂ = 1). The total flow rate was always kept at 35 mL min⁻¹. The products of the reaction were analyzed using a gas chromatograph (Simple Chrom) connected to a TCD detector. CO₂ reforming of methane was conducted at 600 °C for 6 h.

3. RESULTS AND DISCUSSION

3.1. Textural and Structural properties of the solids

The physicochemical properties of the solids are shown in the Table 1. The nitrogen sorption isotherms (not showed) are of type IV, indicating mesoporosity. The surface area of the solids decreased as the La₂O₃ amount increased (≥ 12 wt.%) and this phenomenon effected on the pore volume and diameter. However, no significant variation is observed to La amounts < 6 wt.%. It could be attributed to a La deposition on the mesoporous; as the La₂O₃ content was progressively increased, the pore occlusion results in the agglomeration of La on the solid surface (Barrera et al., 2001).

Table 1 - Surface area (S_{BET}), pore volume (Vₚ), average pore diameter (Dₚ), dispersion of Pt (D_{Pt}), and conversion of methane (C_{CH₄}) of PtₓLA catalysts at 600 °C on dry reforming of methane

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>La₂O₃ wt. %</th>
<th>S_{BET} m²/g</th>
<th>Vₚ cm³/g</th>
<th>Dₚ nm</th>
<th>C_{CH₄} (%)</th>
<th>aCH₄ (μmol CH₄ g⁻¹ s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PA</td>
<td>-</td>
<td>118.3</td>
<td>0.24</td>
<td>6.4</td>
<td>0.6</td>
<td>0.41</td>
</tr>
<tr>
<td>P1LA</td>
<td>0.9</td>
<td>131.9</td>
<td>0.26</td>
<td>6.2</td>
<td>5.2</td>
<td>3.48</td>
</tr>
<tr>
<td>P3LA</td>
<td>3.1</td>
<td>137.5</td>
<td>0.26</td>
<td>5.9</td>
<td>16.5</td>
<td>11.06</td>
</tr>
<tr>
<td>P6LA</td>
<td>5.8</td>
<td>133.7</td>
<td>0.22</td>
<td>5.1</td>
<td>26.7</td>
<td>15.25</td>
</tr>
<tr>
<td>P12LA</td>
<td>11.8</td>
<td>89.9</td>
<td>0.16</td>
<td>5.2</td>
<td>22.1</td>
<td>16.86</td>
</tr>
<tr>
<td>P20LA</td>
<td>19.6</td>
<td>75.3</td>
<td>0.12</td>
<td>5.1</td>
<td>16.6</td>
<td>11.15</td>
</tr>
</tbody>
</table>

* after 5 h of reaction at 600 °C

Assuming that the addition of highly dispersed La₂O₃ particles to the Al₂O₃ carrier and also assuming that Pt species are nanoparticles, one can infer that the textural properties of the solids are kept unchanged (Rocha et al., 2012). Nevertheless, the decrease of the pore volume of the Pt20LaAl (ca. 0.12 cm³/g⁻¹) compared with the value obtained for the Pt1LaAl (ca. 0.26 cm³/g⁻¹) is characteristic of the presence of La₂O₃ within the channels of the mesoporous γ-alumina support, limiting the access to the N₂ molecules during the isotherm adsorption measurements.

The XRD patterns of the solids (Figure 1) showed the characteristic diffractions peaks of γ-Al₂O₃. Indeed, the reflexions detected neither correspond to the platinum nor to other crystalline phases of lanthana, even at a loading of 20 wt.% of the latter oxide. This could be due to Pt and La dispersion on the solid surface.
Figure 1 – XRD spectra of PtxLA catalysts where (x) wt. % of La$_2$O$_3$ content.

Temperature programmed reduction profiles are shown in Figure 2. The La$_2$O$_3$-Al$_2$O$_3$ support reducibility is unlikely (not showed). In contrast, all Pt-containing supports exhibit reductions peaks.

Figure 2 - TPR profiles of the catalysts PtxLA.
TPR measurements evidenced the PtOₓ reduction to Pt⁰ at 236-407 °C range. These peaks are attributed to \([\text{Pt}^{IV} (\text{OH})_x \text{Cl}_y]\) and \([\text{PtO}_x \text{Cl}_y]\) species (Navarro et al., 2005). Additionally, the temperature of reduction of PtOₓ species increased with high La₂O₃ loadings (6 wt.%), probably due to a strong interaction between La₂O₃ and PtOₓ. Furthermore, Pt metal dispersion increases when La₂O₃ content increases on \(\gamma\)-Al₂O₃ surface. These results suggest that for a loading of lanthana \(\leq 6\) wt.% there is a higher dispersion of Pt nanoparticles, which are indeed strongly interacting with La. Thus, it could explain the shift of the appearance of the peak at 407 °C.

All catalysts were active in the dry reforming of methane (Table 1 and Figure 3A).

![Figure 3](image-url)  
**Figure 3** – (A) Methane conversion on Dry reforming of methane at 600 °C over PtₓLa with various La₂O₃ content and (B) Raman spectra catalysts used in the dry reforming of methane for 12h of reaction.

High La₂O₃ content provided an increase in the conversion of methane, reaching a maximum for a 6 wt.% of La₂O₃ (Figure 3A) and then, it decreased for 20 wt.% of La₂O₃ (Table 1). The optimum in La₂O₃ content was due to an adequate balance of lanthana and alumina leading to more active catalysts. Additionally, the higher reducibility of the PtOₓ species by increasing the La content, as revealed by TPR measurements, facilitated the methane and carbon dioxide decomposition on solid surface; as consequence, the gases were totally converted into hydrogen and carbon monoxide, according to reaction 1.

Raman spectra of spent PA, P₁₂LA and P₆LA catalysts (Figure 3B) show bands related to a little amount of graphite structure (i.e, filamentous carbon species) at about 1647 cm⁻¹ and a large amount disordered carbon (i.e, amorphous carbon species) at 1350 cm⁻¹, for the referred spent
catalysts. This is not surprisingly the occurrence of carbon species over La-containing catalysts (Tang et al., 2002) and the disorder-induced planes and graphite, known as D and G bands, respectively are attributed to the bands at about 1351 cm\(^{-1}\) and 1577 cm\(^{-1}\) (Batista et al., 2010). For PA, these bands appear at 1390 and 1650 cm\(^{-1}\). Furthermore, the ratio between ID and IG bands for PA are close to 0.81 that illustrates the large amount of carbonaceous graphite species rather than the disordered ones. In other words, Raman analysis evidences a spinel structure, in which PtO\(_\text{x}\) species are reduced to Pt\(^0\) and thus, CH\(_4\) or CO carbon decomposition favors the carbon growth on the top of the particle.

Nevertheless, P12LA deactivation is not too severe, probably because the carbon species (filaments of carbon) are not in a close contact with the Pt and La particles or La[Pt\(_\text{x}\)O]Pt\(^0\) species are formed; therefore, CO\(_2\) can eliminate this kind of ‘active carbon’ by the gasification of coke and Boudouard reactions (Rostrup-Nielsen, 1984). It is confirmed by the stability of the sample towards coking; consequently, there is a much higher Pto active specie to convert the reactants.

Therefore, over both PA and P6LA, the carbon elimination rate is probably lower than the carbon deposition rate and thus, the carbon amount on catalyst surface is significantly at 600 °C. The ID/IG ratio of P6LA and PA catalysts are respectively 0.46 and 0.81 and this give explanation for their low performance as compared with the P12LA (0.28) analogue. Although P6LA has the textural properties similar to those of P12LA, the formation of labile carbon species, i.e., filaments of carbon on P12LA impedes the deactivation of this solid more slowly, as compared to 6wt% ones.

4. CONCLUSIONS

The above study illustrated the influence of the textural, structural and surface properties on the catalytic activity of Pt/xLa\(_2\)O\(_3\)-Al\(_2\)O\(_3\) catalysts in the dry reforming of methane. TPR and DRX results showed that the increase in La\(_2\)O\(_3\) content from 1 to 6 wt.% produced highly dispersed Pt entities, due to the strong interaction of Pt-O-Al and Pt-O-La bonds. Agglomeration of Pt particles is observed for P12LA and P20LA samples.

Textural and surface properties from N\(_2\) adsorption measurements provide evidence indicating the availability of surface is related to La\(_2\)O\(_3\) addition and it facilitates the Pt dispersion on surface and/or in the mesopores as well as the stability of γ-alumina. [LaPt\(_\text{x}\)O]Pt\(^0\) species are formed by the Pt and La interactions during the dry reforming of methane and activity is increased due to the exposition of CH\(_4\) and CO\(_2\) to the active site, as the La\(_2\)O\(_3\) amounts increased.

La\(_2\)O\(_3\) content lower than 6 wt.% impossibilities the Pt reduction because of the Pt-O-La strong interaction and these catalysts showed a modest performance in the reaction. An optimum in catalytic activity is reached for La\(_2\)O\(_3\) content of 6 wt.% and it suggest the one of the roles of La\(_2\)O\(_3\) was to avoid coking by its reaction with CO\(_2\), thereby allowing the stability of the catalyst to operate for 12 h of reaction whereas 20 wt.% of La\(_2\)O\(_3\) had a detrimental effect in activity.

All results suggest that the metal–support interface and the nature of the support have important roles in the accessibility and stability of Pt sites. [LaPtO\(_\text{x}\)Pt\(^0\)]-like species inhibited the coking specially in case of P12LA catalyst, as evidenced by Raman measurements
5. ACKNOWLEDGMENT

The authors are grateful for the financial support of CNPq and FAPES to this research project.

6. REFERENCES