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### Tailoring the physical and catalytic properties of lanthanum

#### oxycarbonate nanoparticles

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### **Graphical abstract**



### Highlights

Flame spray pyrolysis allows tuning of the properties of La based nanoparticles which may lead to improved catalysts for oxidative coupling of methane (OCM).

Changes in the synthesis parameters not only affected the particle size but also basicity and phase.

Higher C<sub>2</sub> yields were obtained with materials of higher basicity.

A mixture of La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> exhibited better OCM performance than La<sub>2</sub>O<sub>3</sub> only.

#### Abstract

The synthesis of lanthanum oxide and its carbonate analogues has been performed by flame spray pyrolysis (FSP). Two different feeds have been studied: an organic solution and an aqueous/organic microemulsion. A key experimental parameter of FSP, the O<sub>2</sub> dispersion, i.e., the flow rate of the dispersing gas in the FSP nozzle, exhibits an effect on the properties of the materials prepared. Increasing the level of O<sub>2</sub> dispersion led to an increase in surface area and a decrease in mean particle size and basicity when a lanthanum containing organic solution was used as FSP feed. Lanthanum can form different phases, such as oxides, hydroxides, oxycarbonates and carbonates. The increase of O<sub>2</sub> dispersion also produced a phase change, going from a mixture of type Ia and type II  $La_2O_2CO_3$  and  $La_2O_3$  to pure La<sub>2</sub>O<sub>3</sub>. The use of an aqueous/organic microemulsion feed, which had a higher viscosity than the organic feed, resulted in materials with a lower surface area and a higher mean particle size than those prepared using the organic solution at the same  $O_2$  dispersion. In this case a mixture of type II La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> was obtained. The materials were tested for oxidative coupling of methane (OCM). We were able to demonstrate that the OCM performance of the materials could be modified by changing the synthesis parameters. For example, lower O<sub>2</sub> dispersion produced the highest CH<sub>4</sub> and O<sub>2</sub> conversions. We also demonstrated that on ageing the mean particle size remain stable; however, the phases do not, showing a new phase, La(OH)<sub>3</sub>, formation and resulting in an increase in OCM activity. While the OCM performances are modest they do demonstrate the power of this approach for controlled synthesis of lanthanum materials.

**Keywords:** lanthanum oxide, lanthanum carbonate, flame spray pyrolysis, basicity, nanoparticles, oxidative coupling of methane

#### **1** Introduction

Lanthanides show unique electric, optical, magnetic and catalytic properties due to their partially filled 4f shell electronic configuration. In particular, lanthanum has been widely used in different applications and for example, can be found in electrode material for magnetohydrodynamic (MHD) power generation<sup>1</sup>, for solid oxide fuel cells interconnects<sup>2</sup>, special glasses for optical devices<sup>3,4</sup>, and as catalysts, either as a promoters<sup>5</sup>, stabilizers<sup>6</sup> or the active phase<sup>7</sup>. Depending on the application of interest, different solid state compounds of

lanthanum such as oxide, hydroxide, oxycarbonates and carbonate, are used. For example,  $La(OH)_3$  is used as an intermediate to form the oxides or sulfides;  $La_2O_3$  is added to prepare special optical glasses, as it increases density, refractive index and hardness<sup>8</sup>;  $La_2(CO_3)_3$  is used in medicine as a phosphate binder<sup>9-11</sup>; and, lanthanum oxycarbonates have been shown to be active for the oxidative coupling of methane (OCM)<sup>12,13</sup>.

Different techniques have been used to synthesise solid state lanthanum compounds such as the thermal decomposition of La salts<sup>14</sup> and precipitation<sup>15</sup>. Interest has also been shown in synthesising lanthanum based materials as nanoparticles<sup>16-18</sup>. Particle size and morphology are two parameters of high importance that can potentially influence material properties. In particular, it is well known that nanoparticles can have different properties thanks to their particle size. An example of such different behaviour was shown by Balusami et al.<sup>19</sup> who demonstrated that lanthanum oxide nanoparticles exhibited antimicrobial activity, which was not observed for the bulk material. A wide range of methods have been used to produce lanthanum based nanoparticles such as, hydrothermal<sup>16,20</sup>, sol-gel<sup>17</sup> and sonification<sup>21</sup>. However, the scale up of these materials through these techniques may prove to be difficult due to elevated reactant prices and efficiency.

Flame spray pyrolysis (FSP) has been used for the single-step production of powders and the technique allows the production of materials with controlled properties at a high rate<sup>22-24</sup>. This can be achieved by modifying the process parameters and the feed composition. Therefore, FSP could be a good alternative for the preparation of nanoparticles of La<sub>2</sub>O<sub>3</sub> and its carbonate analogues, because it may allow the tuning of the phases and their scale-up.

To our knowledge  $La_2O_3$  and its carbonates have not been prepared by FSP before and in this work the synthesis of lanthanum based materials by this technique has been performed. We show that by changing the synthesis parameters, such as  $O_2$  dispersion and feed composition, the particle size and phase composition of lanthanum materials can be tuned, obtaining pure  $La_2O_3$  and mixtures of this with type II and type Ia  $La_2O_2CO_3$ .

Oxidative coupling of methane to ethylene has attracted significant interest since the early 80s when Keller and Bhasin<sup>25</sup> first investigated catalysts for this reaction. In 1985, Lunsford<sup>2</sup> showed that Li/MgO could give a 19% yield for  $C_2$ , with ethylene as the major product, starting from methane. However, further studies showed catalyst deactivation during time in

stream due to Li loss<sup>26-28</sup>. Since then many catalyst combinations have been studied for OCM with the highest obtained  $C_2$  yields of around 25-30%<sup>29</sup>. The most common catalyst formulations have been oxides based on alkaline earth metals doped with alkali metals and rare earth metals doped with alkali or alkaline earth metals<sup>3</sup>. Several studies have shown that the activity of the OCM catalyst is affected by catalyst structural properties<sup>30,31</sup>. Also basicity and oxygen ion-conductivity, which have been identified as key parameters for this reaction, are influenced by catalyst structural properties<sup>32,33</sup>. The use of lanthanum based materials in OCM has been studied extensively<sup>34-39</sup>. The preparation method has shown to have an effect on the properties and, therefore, the activity of the materials. Choudhary et al.<sup>35</sup> found that the catalyst precursor and calcination conditions used to prepare La<sub>2</sub>O<sub>3</sub> influenced the surface properties, basicity and base strength distribution, and activity and selectivity in the oxidative coupling of methane. A comparison of the reactivity of phases was performed by Taylor et al.<sup>13</sup>. They showed that the starting phase had an effect on the activity and selectivity despite La<sub>2</sub>O<sub>3</sub> being the phase after reaction as the carbonates are not stable under OCM reaction conditions<sup>40</sup>. Therefore, OCM has been chosen as a comparative test reaction to test structure-activity relationships for the lanthanum based FSP materials.

There has been some preliminary work looking at nanoparticles for OCM and Farsi et al. reported in a preliminary study that Li/MgO nanoparticles showed higher CH<sub>4</sub> conversion and C<sub>2</sub> yield compared with the conventional Li/MgO catalyst<sup>41,42</sup>. However, this study only compared one sample of each type of material. Our aim in this work was to test the lanthanum based materials for OCM and to perform a more detailed systematic study into the effect of particle size.

#### **2** Experimental

Two different lanthanum solutions were used as feed for the flame spray pyrolysis to prepare two different series of materials and the conditions used for the experiments are summarised in Table 1:

- An organic solution consisting of lanthanum 2-ethylhexanoate in toluene/2ethylhexanoic acid (99 %, Alfa Aesar) (1:1 in volume) designated FSP-01, -02,-03 and -04.
- A microemulsion consisting of cyclohexane, Igepal CO-520 and an aqueous solution of lanthanum nitrate designated FSP-M1 and -M2.

Lanthanum 2-ethylhexanoate was synthesised using La(NO<sub>3</sub>)<sub>3</sub>·6H<sub>2</sub>O (99.9 %, Alfa Aesar),2ethylhexanoic acid (99 %, Alfa Aesar) and NH<sub>4</sub>OH (35 % (d=0.88), Fisher). A mixture of 2ethylhexanoic acid and ammonium hydroxide was added to ~50 ml of deionised water. Lanthanum nitrate was dissolved in ~75 ml of deionised water and this solution was added slowly to the first solution. 500 ml of deionised water were added with stirring to the cottage cheese like precipitate which was formed. The solid was filtered on a vacuum filter and washed with ethanol several times. The solid was then left to dry at room temperature overnight in an evaporating basin in the fume cupboard, resulting in lanthanum 2ethylhexanoate that could be used to synthesise the materials by FSP.

Flame Spray Pyrolysis was performed using equipment which has been described previously<sup>23</sup> and a diagram of the FSP rig used to prepare the mateials presented in this work is shown in Figure S1 in the Supporting information (SI). The precursor solution, either the organic or the microemulsion solution, was fed into the flame using a syringe pump and dispersed into fine droplets with a nozzle using  $O_2$ , the latter being referred to as  $O_2$  dispersion. The flame was fed with  $O_2$  and CH<sub>4</sub> jets positioned in a ring around the nozzle outlet. Additional  $O_2$  is provided to surround the flame as a sheath and the lanthanum containing solid compounds were collected on a glass fibre filter with the help of a vacuum pump.

BET surface area analysis was performed using a Quanta Chrome Autosorb-1 apparatus using nitrogen as the adsorbate. Prior to analysis, samples were outgassed at 150 °C under vacuum for approximately 24 h. X-ray diffraction data (XRD) were obtained with a Bruker AXS D8 diffractometer and using Cu Kα radiation and the data collected from 10 to 130° 20 with a step size of 0.02°. Ratios of the identified phases and their crystallite sizes were determined by Rietveld refinements using TOPAS (Total Pattern Analysis Solution)<sup>43</sup>. Structural models for La<sub>2</sub>O<sub>3</sub> and the type II polymorph of La<sub>2</sub>CO<sub>3</sub>O<sub>2</sub> are well documented<sup>44-<sup>46</sup>. The type Ia structure was determined by combining documented lattice parameters with suggestions that it is a monoclinic distortion of the tetragonal Bi<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> structure<sup>47,48</sup>. Samples for transmission electron microscopy (TEM) analysis were ground between two glass slides and dusted onto a holey carbon coated Cu TEM grid and a Tecnai F20 transmission electron microscope was used to examine the samples at a 200 kV accelerating</sup>

voltage. X-ray Photoelectron Spectroscopy (XPS) of the FSP materials was measured with a Thermo Escalab 250. The radiation used was monochromatised aluminium K $\alpha$  radiation with a 650 µm spot size. Charge compensation was provided by the in-lens electron flood gun at a 2 eV setting and the "401" unit for "zero energy" argon ions.

Temperature programmed decomposition of the as prepared samples was carried out with a Micromeritics AutoChem II 2920 chemisorption analyser. The samples were heated up to 900  $^{\circ}C(10^{\circ}C/min)$  under a helium flow in a "U" shaped quartz tube. The effluent was analysed with a mass spectrometer, MKS Cirrus 2.

Oxidative coupling of methane (OCM) testing was performed with a high throughput reactor comprising eight quartz reactors (internal diameter = 4 mm, outside diameter = 8 mm). The reaction mixture consisted of CH<sub>4</sub>, O<sub>2</sub> and N<sub>2</sub>. The conditions used were:  $W/F_{CH4} = 2$  kgs/mol, CH<sub>4</sub>/O<sub>2</sub> ratio = 2:1, 10 % N<sub>2</sub> (internal standard) and a temperature programme of: 650, 750, 650, 850 and 650 °C. The ramp to the different temperatures was performed under nitrogen and the results presented in the paper were started to be taken after 2.5 hours. The temperature was controlled with a thermocouple located in one of the reactors containing quartz wool, which was used as a blank reactor to account for the gas phase reactions. Reference to the blank reactor results are given where appropriate in the results section. A Varian CP4900 Micro-GC was used to analyse nitrogen, methane and upup to C<sub>9</sub> products. However, the discussion of this paper has been based on the C<sub>2</sub> products as only traces of C<sub>3</sub> were observed, in particular at high O<sub>2</sub> conversions. Carbon balance was normally around 90 %, however under extreme conditions (CH<sub>4</sub> converions <15 % and complete O<sub>2</sub> conversion) the carbon balance was lower. Drawing conclusions at these extreme conditions was avoided.

#### **3 Results and discussion**

#### 3.1 Nanoparticle synthesis

It is well known that  $La_2O_3$  tends to react at room temperature with water vapour, forming hydroxides which can then react with the atmospheric  $CO_2$  to form carbonates<sup>49</sup>. This could affect the shelf stability of these materials and for this reason the stability when stored was also studied. The characterisation of the fresh samples and samples aged for 24 months stored in vials is presented.

#### 3.1.1 Particle size and surface area

TEM images of both the organic and microemulsion samples showed sphere like materials, see Figure 1, with different mean particle size distributions for all the materials. The  $O_2$  dispersion had an influence on the mean particle size for the organic solution derived materials: the higher the  $O_2$  dispersion the smaller the droplet size and ,hence, the smaller the mean particle size<sup>23</sup>. Using the microemulsion instead of the organic solution with the same  $O_2$  dispersion, 8 l/min, resulted in larger mean particle size, FSP-M1 (40.4 nm) and FSP-M2 (35.6 nm). This difference in size is probably due to the different viscosity of the feed, since the microemulsion was more viscous than the organic solution. An increase in viscosity would be expected to slow down the atomization process by increasing the surface stability of the droplet. The liquid is then capable of withstanding the shear force from the dispersion gas<sup>50</sup> producing bigger droplets and therefore materials with higher mean particle size. The BET surface area of all materials correlated well with the TEM results, where an increase in mean particle size showed a decrease in the surface area, see also Figure 2.

TEM analysis performed on the aged samples showed similar mean particle sizes compared to sizes obtained for the fresh ones; see Table 2, indicating that standing for 24 months has not resulted in significant particle growth.

#### 3.1.2 Phase

#### 3.1.2.1 Fresh samples

XRD analysis of the organic and microemulsion samples revealed the presence of a number of different phases such as hexagonal La<sub>2</sub>O<sub>3</sub>, and type Ia and type II La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, Table 3. The XRD patterns are presented in Figure S2-7 in the Supporting information. Type Ia and type II La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> are stable intermediates observed in the thermal decomposition of La<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> to form the thermodynamically most stable La<sub>2</sub>O<sub>3</sub> phase. The formation of the oxycarbonate phases has been reported previously between 450-550 °C<sup>21,51</sup>, however, higher temperatures between 700-900 °C are needed to form La<sub>2</sub>O<sub>3</sub><sup>51,52</sup>. There are a number of factors including the heat transport rate through the droplet, the residence time in the flame, oxygen availability or phase thermodynamics that may determine which phases are ultimately produced during FSP. It is noticeable, however, that the O<sub>2</sub> dispersion appears to be the most significant parameter in the control of the phase produced, see Figure 3. At lower O<sub>2</sub> dispersions, such as with samples FSP-O2 and 1, the formation of type Ia La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> phase is observed even

including some type II  $La_2O_2CO_3$  at the lowest  $O_2$  dispersion; in contrast at higher dispersions only hexagonal  $La_2O_3$  is formed. Furthermore, the amount of hexagonal  $La_2O_3$ phase increases with  $O_2$  dispersion. The suggested explanation for this is that increasing  $O_2$ dispersion leads to smaller droplet sizes of the liquid as it is injected into the flame which will lead to higher temperatures during the lanthanum 2-ethylhexanoate oxidation/decomposition process and a more oxidising environment for oxide formation. This means that as the droplet size decreases the extent of intermediate phase formation decreases and the formation of the thermodynamically most stable phase becomes dominant.

XRD shows that the materials prepared using the microemulsion feed comprise type II La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and hexagonal La<sub>2</sub>O<sub>3</sub> with different ratios. Sample FSP-M1 contained a slightly higher amount of type II La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, 63.6%, than sample FSP-M2, 42.2 %. In addition to the significant effect of the O<sub>2</sub> dispersion seen for the materials prepared with the organic solution it is clear for the FSP-M that the precursor solution has an effect as well. For example, compare the FSP-M samples and FSP-O3 which were all prepared using the same O<sub>2</sub> dispersion and yet show a different phase composition. This suggests that the presence of oxide carbonates in the FSP-M samples is due to an additional factor such as the precursor composition. The microemulsion samples contain water which will lower the flame temperature and result in a different thermodynamic equilibrium composition comprising a mixture of intermediate phases and La<sub>2</sub>O<sub>3</sub>. Additionally the presence of water will also allow more liquid phase interactions to take place during the nucleation stage of particle formation immediately prior to evaporation and combustion.

#### 3.1.2.2 Aged samples

XRD analysis was repeated on all samples 24 months after being prepared, see Table 4. The XRD patterns are presented in Figure S2-7 in the Supporting information . These showed that, for the samples prepared using the organic solution, the La<sub>2</sub>O<sub>3</sub> had reacted with atmospheric water to form the La(OH)<sub>3</sub>. However, the samples prepared with the microemulsion feed, FSP-M1 and FSP-M2, showed no or, at most, a small amount of La(OH)<sub>3</sub>. An increase of amorphous phase was observed for the samples initially containing La<sub>2</sub>O<sub>3</sub> and type Ia La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>, i.e., FSP-O2, FSP-O3 and FSP-O4. No amorphous phase was observed for the samples containing type II La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>.

XPS performed on the aged samples shows the presence of two O1s signals for all of the samples. The O1s signal at 528 eV corresponds to  $O^{2-}$  species from lanthanum oxide and the one at 531 eV could be assigned to hydroxyl groups or to carbonates<sup>39,53</sup>. Because of the presence of a C1s signal at 289 eV, which corresponds to carbonates<sup>54</sup>, the signal at higher binding energy from the O1s could be assigned to the carbonate oxygen. Adventitious carbon can be found at 284.6 eV<sup>54</sup>. The XPS results suggest the presence of carbonates on the surface of all the samples. These results differ from the ones obtained with the XRD, where aged sample FSP-O3 and FSP-O4 showed the presence of only La(OH)<sub>3</sub>. XRD shows the composition of the bulk crystalline material with a particle size bigger than 2 nm while XPS shows the composition of the s-form and is able to also detect amorphous material in addition to crystalline phases which suggests that the particles have a surface layer of amorphous or semi crystalline (particles less than 2nm) lanthanum carbonate<sup>55</sup>. The La3d signal confirms the presence of  $La^{+3}$ . This signal includes the main peak (La 3d cf<sup>0</sup>), the satellites (La 3d cf<sup>1</sup>), the plasmons and the auger peaks (Figure 4). Previous work by Sunding et al.<sup>53</sup> reported on the relative intensities between the different peaks for La<sub>2</sub>O<sub>3</sub> and La(OH)<sub>3</sub> which can be used to aid the interpretation of the phases. For simplification we have looked into the relative position of the La 3d  $cf^0$  and the La 3d  $cf^1$  L bonding ( $\Delta BE$ ) for all the samples and also for bulk La<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> and La(OH)<sub>3</sub>. The reported  $\triangle$ BE value for La<sub>2</sub>O<sub>3</sub> is 4.9 and for La(OH)<sub>3</sub> is 3.9 eV which are similar to the ones obtained for the pure materials measured in our equipment, see Table 5. The value for the  $La_2(CO_3)_3$  reference material is similar to that for the hydroxide, making it difficult to differentiate these. When comparing the relative peak positions for the bulk materials and the FSP materials a clear trend can be observed. The samples prepared using lower O<sub>2</sub> dispersion, FSP-O1 and FSP-O2, have similar relative peak position to the La<sub>2</sub>(CO<sub>3</sub>)<sub>3</sub> and La(OH)<sub>3</sub> reference materials. Instead, for the ones with higher O<sub>2</sub> dispersion, FSP-O3 and FSP-O4, their values started to be similar to the relative peak position of the La<sub>2</sub>O<sub>3</sub>, being FSP-O4 the closest. The microemulsion samples, FSP-M1 and FSP-M2, appear to be close to the oxide. These results suggest that on FSP-O4, FSP-M1 and FSP-M2 the oxide is stabilised on the surface.

#### 3.1.3 Basicity

The results obtained from the decomposition of the aged materials under helium are given in Figure 5 and show that two types of carbon(ate) are present, surface (<500 °C) and structural

(>500 °C). The amounts observed can be used as an indicator of the strength of the basic sites present on the material. The decomposition temperature of a carbonate has been used previously to assess the basicity of its oxide<sup>56</sup>. More basic oxides will tend to release CO<sub>2</sub> only at higher temperatures due to a stronger interaction. The strength of the basic sites can be classified as a function of the temperature at which CO<sub>2</sub> release is observed: 50-250 °C (weakly basic sites), 250-600 °C (intermediate basic sites) and 600-950 °C (strongly basic sites). Differences can be observed between the samples in the sites of weak and intermediate basic strength, where an increase of the O<sub>2</sub> dispersion produces samples with higher amounts of these sites, see Table 6. Interestingly, FSP-O1, which is the sample with the lowest O<sub>2</sub> dispersion (2 l/min), only exhibits one peak (254 °C) at the low temperatures, instead of three. All four samples exhibit a single, pronounced peak at high temperatures which corresponds to the strongly basic sites. Only FSP-O1 and FSP-O2 showed the presence of carbonates by XRD. Nevertheless, the presence of carbonates in all the samples is also observed by XPS. The decomposition temperature of the strong basic sites<sup>57</sup> is much higher on the sample prepared with the lowest O<sub>2</sub> dispersion. This sample also has the largest particles with a mean diameter amounting to 40 nm, suggesting that a smaller particle size leads to a weaker basicity. This is in agreement with the results reported by Montero et al.<sup>58</sup> on MgO, who showed that the basicity of MgO decreased with decreasing particle size.

#### 3.1.4 Summary on the materials stability

The samples prepared using high O<sub>2</sub> dispersion, i.e., FSP-O3 and FSP-O4, which presented the smallest mean particle size and are only composed of a single phase, were not stable over 24 months and transformed from the La<sub>2</sub>O<sub>3</sub> into the hydroxide. The same behaviour was observed for sample FSP-O2, which only contained a small amount of type Ia La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>. However, the La<sub>2</sub>O<sub>3</sub> present in FSP-O1, FSP-M1 and FSP-M2, samples that contained mainly carbonates, were more stable and even XPS showed it to be stable on the surface. However, changes of the phase were observed and this did not affect the mean particle size of the materials.

#### 3.2 OCM testing

#### 3.2.1 Fresh samples

#### 3.2.1.1 Stability of nanomaterials to temperature

Lanthanum based nanomaterials were tested for OCM at different temperatures to address, among others properties, material thermal stability, see Figure 6. The materials prepared from the organic solution showed low activity at 650 °C. The effect on the materials to the exposure of high temperatures can be observed in Figure 7. The thermal history for the samples prepared with the organic solution is significant even after reaching 750 °C. However, smaller differences are observed for the samples prepared using a microemulsion. Surface area was not looked at in the spent catalysts because a limited amount of catalyst was available. However, when looking at the spent catalyst by TEM, aggregation of the particles can be observed producing flake like materials, see Figure 8, which were not there on the catalyst as prepared. The FSP-ME samples also suffer aggregation but it does not have such an impact to the activity. This suggests that for these materials the aggregation and therefore change in morphology, between spheres and flakes, does not play a dominant role in defining OCM activity. As expected, an increase in OCM activity is observed for these materials when the temperature is increased. However, at 850 °C the C<sub>2</sub> yield from the blank reactor, i.e., 7.9 %, exceeds that from the FSP-O samples except for the one prepared with 2 l/min of O<sub>2</sub> dispersion.

The materials prepared using an aqueous/organic microemulsion mixture as a feed were tested under the same conditions, see Figure 6, and for these materials a decrease in the  $C_2$  yield is observed with increasing of temperature which is not the expected trend. The reason for this phenomenon could be that the system has already reached its maximum performance even at lower temperatures with 100 % O<sub>2</sub> conversion. At 650 °C sample FSP-M1 shows a significant  $C_2$  yield, i.e., 11.5 %. However, when the system is cooled down again to this temperature after reaching 750 and 850 °C a decrease in the  $C_2$  yield is observed. These changes on the activity depending on the thermal history can be observed as well with the materials prepared using the organic solution but is not observed with the sample FSP-M2.

#### 3.2.1.2 Properties- OCM activity relationship

With increasing  $O_2$  dispersion used in catalyst synthesis, i.e., from FSP-O1 to FSP-O4, a decrease in the  $C_2$  yield and CH<sub>4</sub> conversion is observed. The  $O_2$  conversion also decreases with increasing  $O_2$  dispersion which suggests that the capacity of the catalyst to activate the  $O_2$  is decreasing. At the lowest  $O_2$  dispersion the ethylene production exceeds that of ethane and, additionally, some propylene is formed. The behaviour observed for this catalyst prepared at the lowest  $O_2$  dispersion, FSP-O1, is clearly starting to differentiate from the other FSP-O samples and getting closer to the performance of the FSP-M samples.

It is well known that an increase in surface area can have a positive effect on the catalyst activity as more active sites are available. In particular for OCM, previous work has shown that when increasing the surface area an increase of the activity is observed. Thybaut et al.<sup>59</sup> reported simulation data for the catalyst Sn/Li/MgO in which an increased surface area resulted in an increased CH<sub>4</sub> conversion. There will be an optimum surface area to achieve the highest  $C_2$  yield and this is because with increasing surface area the catalyst will also accelerate the further reaction of  $C_2$  products decreasing the yield to  $C_2$ . Figure 9 represents the CH<sub>4</sub> conversion versus surface area of all the prepared catalysts tested at 750 °C. The activity of the empty reactor at 750 °C temperature is included for comparison. A decrease in the CH<sub>4</sub> conversion is observed with an increase of surface area which is the opposite trend to the one expected from literature. Therefore, the observed trend should be due to other factors, such as, particle size, phase or basicity and these other factors are discussed below.

The particle size has an effect on the OCM activity. The materials with a smaller mean particle size (FSP-O3 and FSP-O4) have lower activity, 16.8 %, and the ones with the larger mean particle size (FSP-M1 and FSP-M2) show the higher activity, 44 % (Figure 6). However, as mentioned before, Farsi et al.<sup>41,42</sup> reported that Li/MgO nanoparticles were more active than a bulk catalyst. Also given the trend found at the microscale by Thybaut et al.<sup>59</sup> it should be expected to reach higher activity at lower particle size. In our case, this is the opposite because the change in particle size also is accompanied by other structural changes.

The samples containing type II  $La_2O_2CO_3$ , FSP-M1 and FSP-M2, demostrate the higher OCM activity, followed by FSP-O1, which contains traces of type II  $La_2O_2CO_3$  and its major phase is the type Ia  $La_2O_2CO_3$ . FSP-O2 shows also similar OCM activity and this contains lower amounts of  $La_2O_2CO_3$ . The materials showing the lowest OCM activity, FSP-O3 and

FSP-O4, only contain the hexagonal La<sub>2</sub>O<sub>3</sub>. Taylor et al.<sup>13</sup> reported that OCM activity was dependent on the phase as follows, even if after reaction La<sub>2</sub>O<sub>3</sub> was the only phase present: type II La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> > type Ia La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> > La(OH)<sub>3</sub> > La<sub>2</sub>O<sub>3</sub>. This suggests that the reason for the increase in activity is due to the transformation in phase from hexagonal La<sub>2</sub>O<sub>3</sub> to type Ia La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and then to type II La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub>.

Another important property that materials active for OCM have in common is their basicity which is known to enhance the OCM activity because previously reported mechanisms suggest that methane activation occurs on a basic  $O^{-2}$  via hydrogen abstraction<sup>60</sup>. Montero et al.<sup>32</sup> reported that the basicity of MgO increased with increasing particle size. The same effect may govern the observations on the materials described in this paper and the results presented from the decomposition of the carbonates confirm that the materials with lower mean particle size release  $CO_2$  at lower temperatures, which is related to lower basicity. Therefore, a decrease in activity could be related to a decrease in basicity of the materials obtained which could also be related to the phase present.

#### 3.2.2 Aged samples

#### 3.2.2.1 Properties- OCM activity relationship

The aged samples showed similar sensitivity to the thermal history as the fresh samples (Figure 7) and higher  $C_2$  yield at lower temperatures compared to the fresh samples. Due to their high activity, 100 % O<sub>2</sub> conversion was observed (Figure 10), making comparison between the aged materials not possible. In fact, the CH<sub>4</sub> conversion at 650 °C is comparable to that obtained at 850 °C with the fresh samples. As already discussed, this difference in activity cannot be due to changes in morphology or particle size because TEM shows that when the samples are aged they remain spherical with a similar mean particle size. The explanation for the increase of activity can be found, as for the fresh samples, in the phase. XRD and XPS suggest that the La<sub>2</sub>O<sub>3</sub> from the fresh samples has reacted with the atmospheric water and CO<sub>2</sub> to form the hydroxide/carbonate. This happened even if the samples were stored in an air tight bottle and had minimum contact with the atmosphere. This new phase now present in the aged samples is more active than the oxide as also suggested by Tylor<sup>13</sup> in previous studies. Therefore, the preparation of materials containing carbonates by FSP should be further studied. The aim would be to obtain flame conditions in which carbonates are formed, so high temperatures in the flame should be avoided.

#### Conclusions

FSP has produced a series of materials that show a number of changes with increasing  $O_2$  dispersion: surface area, phase and basicity. The catalytic properties of the final materials are dependent on a combination of all three parameters with surface area being less influential than phase and basicity. Two different feeds have been used to prepare lanthanum oxide and its carbonates analogues. For these materials a phase change was observed by XRD, from a mixture of type II and type Ia La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and La<sub>2</sub>O<sub>3</sub> to pure La<sub>2</sub>O<sub>3</sub>, which could be due to an increase in the O<sub>2</sub> availability. The use of a more viscous feed, the microemulsion, resulted in the production of materials with larger mean particle sizes and, therefore, smaller surface areas. The XRD for these materials was shown to be a mixture of type II La<sub>2</sub>O<sub>2</sub>CO<sub>3</sub> and La<sub>2</sub>O<sub>3</sub>.

Despite the lower surface area the materials containing a mixture of type II and type Ia  $La_2O_2CO_3$  and  $La_2O_3$  exhibited  $C_2$  yields of around 12 % at 750 °C, instead the materials containing only  $La_2O_3$  presented much lower  $C_2$  yields, 4 %. The materials showing the higher  $C_2$  yields were also the materials that presented higher  $CO_2$  decomposition temperatures which implies higher basicity. The same trend was observed for the  $C_{2=}/C_2$  ratio which was higher for the materials with higher amounts of carbonates.

This work has shown that FSP can be used to tune the properties of La<sub>2</sub>O<sub>3</sub> based nanoparticles and samples anywhere within the three dimensional experimental space defined by surface area, phase and basicity and this flexibility may lead to improved catalysts for OCM.

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#### **Figure captions**

Figure 1. TEM images for the samples prepared using the organic solution and the microemulsion.

Figure 2. O<sub>2</sub> dispersion effect on the BET surface area and mean particle size measured by TEM.

Figure 3. Phase distribution depending on the O<sub>2</sub> dispersion.

Figure 4. XPS spectra from the La 3d region for the sample FSP-O2.

Figure 5. CO<sub>2</sub> measured during decomposition of the materials prepared using an organic solution.

Figure 6. OCM results for the materials prepared by FSP with different O<sub>2</sub> dispersion.

Figure 7. C<sub>2</sub> yields for fresh (line) and aged (dotted line) samples at 650 °C. 1) First time at 650 °C; 2) after reaching 750 °C; and, 3) after reaching 850 °C.

Figure 8. TEM images for the materials prepared by FSP after OCM reaction.

Figure 9. CH<sub>4</sub> conversion at 750 °C is shown against surface area for the materials prepared using the organic solution and the microemulsion.

Figure 10. OCM results for the aged samples prepared at different O<sub>2</sub> dispersion.

Fig.1









#### Fig.4











Fig.8







Solution	Sample Name	[La] (M)	Precursor Feed Rate (ml/min)	O2 Dispersion (l/min)
Organic Solution	FSP-O1, 2, 3 and 4	0.2	5	2,5,8 and 10
Aqueous/Organic Microemulsion	FSP-M1 and 2	0.06- 0.12	3-5	5

#### Table 1. Preparation details for the lanthanum nanomaterials.

\*O<sub>2</sub> sheath = 5 l/min; flame  $O_2$  = 3.2 l/min and flame  $CH_4$  = 1.5 l/min

	Fresh sample (nm)	Aged sample (nm)	
FSP-O1	38.44 (±22.75, <i>n</i> =64)	-	
FSP-O2	14.79 (±3.39, n=25)	14.9 (±6.6, n=27)	
FSP-O3	9.94 (±3.07, <i>n</i> =43)	11.1(±3.1, n=28)	
FSP-O4	11.95(±2.38, n=25)	11.6 (±3.1, n=28)	
FSP-M1	33.35 (±11.61, <i>n</i> =71)	57.9 (±35, <i>n</i> =18)	
FSP-M2	21.21 (± <b>7.16</b> , <i>n</i> =38)	28.3 (±5.5, <i>n</i> =22)	

Table 2. Mean particle size of the fresh and aged samples obtained with TEM.

\*n is the number of particles used to calculate the mean particle size.

	Phase	Crystanite Size (nm)
FSP-O1	$La_2O_3$	21 (±3)
	Type II La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	10
	Type Ia La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	25 (±1)
FSP-O2	$La_2O_3$	9.4 (±4)
	Type Ia La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	5
FSP-O3	$La_2O_3$	8.2 (±3)
FSP-O4	$La_2O_3$	7.5 (±3)
FSP-M1	$La_2O_3$	60 (±2)
	Type II La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	19 (±1)
FSP-M2	$La_2O_3$	65 (±2)
	Type II La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	16 (±2)

# Table 3. Crystallite size for the different phases present in the materials prepared.PhaseCrystallite Size (nm)

<b>*</b>	FSP	-01	FSP	-02	FSP	-03	FSP	-04	FSP	<b>-M1</b>	FSP	<b>-</b> M2
	$\mathbf{F}$	Α	F	Α	F	Α	F	Α	F	A*	F	Α
La <sub>2</sub> O <sub>3</sub>	29		83		100		100		37	$\checkmark$	59	44
Type II La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	16	18							63	$\checkmark$	41	37
Type Ia La <sub>2</sub> O <sub>2</sub> CO <sub>3</sub>	56	63	17	24								
La(OH) <sub>3</sub>		19		76		100		100		$\checkmark$		
Amorphous	~0	~0	7	34	18	53	24	62	~0		~0	~0

Table 4. Phase composition obtained with XRD for the fresh (F) and aged (A) FSP-O and FSP-M samples.

\* The amounts of each phase could not be determined due to interference with the PTFE holder as low amounts of sample were available.

	La 3d <u>c</u> 4f <sup>0</sup> (eV)	La 3d <u>c</u> 4f <sup>1</sup> <u>L</u>	ΔBE (eV)
		bonding (eV)	
La <sub>2</sub> O <sub>3</sub>	834.44	839.39	4.95
La <sub>2</sub> (CO <sub>3</sub> ) <sub>3</sub>	836.13	840.08	3.95
La(OH) <sub>3</sub>	836.14	839.69	3.55
FSP-O1	836.04	839.64	3.6
FSP-O2	835.92	839.53	3.61
FSP-O3	835.86	839.75	3.89
FSP-O4	835.04	839.69	4.65
FSP-M1	834.81	839.34	4.53
FSP-M2	835	839.52	4.52

Table 5. Peak positions for the La 3d main peaks ( $\underline{c}4f^0$  states) and satellites ( $\underline{c}4f^1$ ). Also the relative position of these peaks is given.

	Weak	Intermediate 1	Intermediate 2	Strong
FSP-O1	-	251	-	680
FSP-O2	-	251	274	647
FSP-O3	90	278	272	658
FSP-O4	84	278	262	647

#### Table 6. CO<sub>2</sub> decomposition temperature for the samples prepared at different O<sub>2</sub> dispersion.