# SOLUTION COMBUSTION SYNTHESIS BOOSTS CERIA ACTIVITY TOWARDS DIESEL SOOT COMBUSTION

Pietro Palmisano, Nunzio Russo, Debora Fino, Claudio Badini, Politecnico di Torino, Torino, Italy

#### Abstract

Nano-sized particles of ceria with high surface area were processed by solution combustion synthesis (SCS) and their catalytic activity towards combustion of carbonaceous materials was compared with that obtained by simple thermal decomposition of cerium nitrate, exhibiting the same specific surface area. These two kinds of ceria powders were tested, by DTA and temperature programmed combustion of diesel soot and a commercial carbon.

Ceria processed by SCS was found to be more active than its counter part since it could decrease significantly both combustion activation energy (from 115 to 111 kcal/mol) and TPC-plot peak temperature (from 466 to 405 °C) of diesel soot.

The mechanism of the catalytic reaction of combustion was investigated by TPD/R experiments. Likewise other combustion catalysts acting as oxygen pumps, also ceria can exchange limited amounts of oxygen even below 300°C, the SCS-synthesized one showing a superior  $O_2$  release at low temperatures ( $\leq 450$ °C). Finally, the effect of specific aging protocols (thermal treatment at 600°C for 96 hours) in the presence of potentially deactivating species present in diesel exhaust gases (SO<sub>2</sub> and water), was also studied showing that the here proposed materials suffers from less significant ageing than Ce(NO<sub>3</sub>)<sub>3</sub>-derived ceria.

## Introduction

The catalytic activity of cerium oxide towards the combustion of carbonaceous materials at low temperature has been widely investigated [1, 2], mainly with the aim of developing methods capable of reducing diesel soot emissions. Catalysts suitable for promoting low temperature combustion of carbonaceous materials may indeed be applied in the traps designed for the abatement of diesel particulate, which is one of the most harmful pollutants emitted by diesel engines. Since the exhaust gases do cool down to 180-400°C along the pathway from the engine to the silencer, it is mandatory to develop catalysts active enough to ignite soot within the above temperature range. These catalysts can be either deposited on a ceramic support (honeycomb or foam shaped filtering devices) thus obtaining a catalytic trap, or generated inside the combustion chamber by using a proper metal-organic precursor of the catalyst, that must be added to the fuel [1]. In this last case the catalyst particles get in tight contact with soot and are carried by exhausts towards the filtering device where soot combustion occurs [1, 3]. Several kinds of catalysts have been tested: perovskite type oxides [4], spinel type oxides [5], alkaline or heavy metal oxides [6-11], mixtures of halides with vanadates or molibdates [12-16], precious metals [17, 18]. A comparison among the performance of the different catalysts proposed to date should be made bearing in mind that not only the catalytic activity, but several other catalyst characteristics must be taken into account: thermal stability, chemical reactivity towards both the ceramic supports and the chemical species contained in the emissions, cost, etc.

Ceria is thought to display appreciable oxidation activity, fair thermal stability, poor chemical reactivity with respect to many ceramic supports and the main diesel emission components (water vapour, carbon and nitrogen oxides). Ceria is actually worldwide adopted as a promoter of most automotive catalysts [19].

The catalytic combustion of diesel particulate is a process based on a heterogeneous reaction involving solid particles of soot, gaseous oxygen and, of course, the solid catalyst. In order to promote the combustion, the catalyst must get in tight contact with soot particles, which means that the adoption of small particles of catalyst can be quite convenient and help increasing the number of contact points between the two counter parts. Furthermore, also the interaction between the catalyst and the oxygen contained in diesel exhausts is believed to play an important role in the combustion of soot, in particular when the catalyst acts as an oxygen pump [20] and even promotes oxygen spill-over [21].

Hence, the catalytic activity is related to the chemical composition and the structure of the catalyst as well as to the size of the catalyst particles and their specific surface area. For instance, ceria produced *"in situ"* within the engine combustion chamber by decomposition and oxidation of organometallic fuel additives is believed to show an enhanced activity owing to the nano-sized catalyst particles [1].

Nano-structured catalysts with high surface area can be also prepared by solution combustion synthesis (SCS) [22]. This synthesis method involves a self-sustaining strongly exothermal reaction between a sacrificial fuel and nitrates, that act as precursors of the final product. All these reactants are dissolved in water and the resulting solution is heated up to a temperature (between 300 and 700°C) suitable to ignite the whole process. After ignition the reaction quickly goes on spontaneously, due to the heat evolved by the chemical reaction itself. In such a way a ceramic powder made of agglomerates of very small particles (less than one micrometer in size), showing high porosity and high specific surface area, can be rapidly obtained.

Generally speaking, combustion synthesis can be considered as a cheap, energy saving and fast route to obtain nano-structured powders of oxides; for these reasons this technique has been widely applied to the preparation of a great number of different compounds [23].

The combustion synthesis of fine particles of ceria was investigated since 1990 [24], but only more recently a method suitable for the simultaneous synthesis and deposition of ceria on a ceramic honeycomb (and then for processing catalytic traps) has been developed [25].

In this work, the effect of size and surface area of ceria particles on soot combustion kinetics has been investigated with reference to different kinds of carbonaceous materials (diesel soot, Printex U). Moreover, the effectiveness of the nano-structured SCS-synthesized ceria powder has been compared to the performance of a ceria catalyst obtained by thermal decomposition of nitrate, a typical commercial method. Also the reaction mechanism has been studied and related to ceria specific surface area.

Finally, the stability of the catalysts produced, aged at different operating temperatures and gaseous atmospheres (dry, wet and  $SO_2$ -laden air) was carried out. On the basis of the obtained results, the suitability of the mentioned catalysts for application in the treatment of actual diesel exhaust will be finally discussed.

## Experimental

### Catalyst preparation

Ceria has been prepared by SCS from an aqueous solution of cerium nitrate (acting as an oxidizer, Aldrich 99% purity) and urea (acting as a sacrificial fuel, Aldrich 99% purity). According to this method the reagents are dissolved into distilled water and this solution is placed into an oven kept

at a constant temperature (600°C). The solution is quickly brought to boil; it then froths and swells until chemical reaction starts. Combustion is over in a few seconds, resulting in easily-crumbling foam of nano-sized particles with large specific volume and surface area [26].

Combustion synthesis between cerium nitrate and urea occurs according to the following overall reaction which gives rise to a ceria powder and gaseous species:

 $6 \operatorname{Ce}(\mathrm{NO}_3)_3 + 14 \operatorname{CO}(\mathrm{NH}_2)_2 \to 6 \operatorname{CeO}_2 + 14 \operatorname{CO}_2 + 23 \operatorname{N}_2 + 28 \operatorname{H}_2\mathrm{O}$ (1)

The whole reaction can be formally regarded as the combination of two different contributions:

$$2 \operatorname{Ce(NO_3)_3} \rightarrow 2 \operatorname{CeO_2} + 7 \operatorname{O_2} + 3 \operatorname{N_2}$$

$$2 \operatorname{CO}(\mathrm{NH}_2)_2 + 3 \operatorname{O}_2 \rightarrow 2 \operatorname{CO}_2 + 4 \operatorname{H}_2\mathrm{O} + 2 \operatorname{N}_2$$

The exothermic reaction (3), namely urea combustion, provides the heat necessary to the completion of decomposition reaction (2), i.e. the endothermic transformation of nitrate into the desired oxide.

(2) (3)

Cerium oxide obtained by thermal decomposition of  $Ce(NO_3)_3$  in a oven kept at a constant temperature of 600°C for 30 min was also used as a reference catalyst. The temperature and duration of this decomposition treatment have been tuned to obtained exactly the same BET specific surface area of the SCS-synthesised ceria, in order to set a proper basis for a comparison.

Both ceria obtained by combustion synthesis and thermal decomposition have been firstly submitted to physical and chemical characterization.

### Fresh/aged catalyst characterization

The catalysts were analysed by X-ray diffraction (PW1710 Philips diffractometer equipped with a monochromator, Cu-K $\alpha$  radiation) in order to asses their purity, cristalline structure and approximate crystal grain size.

Field Emission Scanning Electron Microscope (FESEM - Leo 50/50 VP with GEMINI column) was employed to analyze the microstructure of the crystal aggregates of the catalysts as prepared and after aging.

The BET specific surface area of the catalysts has been finally evaluated from the linear parts of the BET plot of the  $N_2$  isotherms, using a Micromeritics ASAP 2010 analyzer.

Indications on the pore size distribution of the compared materials has been obtained from the BET  $N_2$  desorption plots.

#### Carbonaceous materials

The catalytic activity of ceria was investigated with reference to combustion of diesel soot and a carbon black.

A commercial carbon (PrintexU by Degussa) was adopted as an example of a carbonaceous material that, contrary to soot, contains much less adsorbed hydrocarbons (5 wt%), as pointed out by Neeft and coworkers [27].

Soot was collected onto a filter positioned at the outlet of a diesel engine (Kubota D 1005-E, which can exploit 23.5 HP at 3000 rpm). This latter carbonaceous material was characterized by using a TGA equipment (Mettler-Toledo TGA-SDTA-851) in order to measure the percentage of moisture, hydrocarbons and ashes. Elemental analysis revealed a carbon content of 73.50 wt%, as much adsorbed hydrocarbons as 18.75 wt% and the presence of 7.75 wt% moisture.

### Catalytic activity tests

The catalytic activity has been tested in a temperature-programmed combustion (TPC) apparatus. This equipment consists of a fixed bed inserted in a quartz microreactor (i.d.: 4 mm). The fixed bed was prepared by mixing 50 mg of a 1:9 by weight mixture of carbon (namely soot or

PrintexU) and powdered catalyst treated in a colloidal mill for 15 minutes, with 150 mg of silica pellets (0.3-0.7 mm in size); these last inert pellets were added in order to reduce the specific pressure drop across the reactor and to prevent thermal runaways. These tight contact conditions allow good reproducibility which is a conditio sine qua non to draw reliable comparisons between the activity of different catalysts. However, these contact conditions are representative of the real catalyst-soot contact conditions only in the aforementioned case of fuel-additive-derived catalysts. Loose contact conditions obtained by gentle shaking of soot and catalyst powders in a vessel provide indeed a better approximation of the contact conditions of soot accumulated in a catalyst-deposited trap [21]. For this reason, a TPC run was also performed with a loose mixture of diesel soot and the best performing catalyst (the SCS-synthesized one).

The TPC reactor temperature was controlled through a PID-regulated oven and it was increased during a TPO run from 200 to 700°C at a 5°C/min rate, under an air flow of 100 Nml/min. The analysis of the outlet gas of the reactor was performed by means of a CO<sub>2</sub>/CO NDIR analyzer. A computer was used to record both the fixed-bed temperature (measured by a thermocouple put nearby the sample) and the concentration of CO<sub>2</sub> in the outlet gas as a function of time (i.e. vs. the programmed temperature). The temperature corresponding to the CO<sub>2</sub> concentration peak (Tp) was taken as an index of the catalytic activity of each tested catalyst. In every case the formation of just a small amount of CO was observed, since the carbon conversion to CO<sub>2</sub> was higher than 97%. The lower the T<sub>p</sub> value the higher the capability of the catalyst to promote a complete combustion with high rate even at low temperature.

#### Activation energy of combustion reaction

Soot and PrintexU are expected to burn in air according to reactions showing different activation energies; these activation energies must decrease when a proper catalyst is adopted, and the activation energy decrease is another good index of the catalyst activity. The Ozawa method [28, 29] proved to be well suitable for calculating activation energy starting from experimental results obtained by differential thermal analysis (DTA). DTA runs were performed by using a Perkin-Elmer equipment in the temperature range from 50 to 720°C with different heating rates (2, 4 and 8 °C/min) under an air flow (100 Nml/min).

In order to evaluate the activation energy for non-catalysed combustion reactions 10 mg of carbonaceous material (PrintexU or diesel particulate) were submitted to DTA runs with different heating rates.

The catalyst effect on combustion reaction was investigated by repeating DTA runs, carried out using samples of 10 mg of a mixture 2:1 by weight of catalyst/carbon (previously mixed in a colloidal mill for 15 minutes).

Proper integrations of the DTA plots allow to measure the temperatures corresponding to different percentages of carbonaceous material burned in each experimental condition adopted for DTA analysis (heating rate, kind of carbonaceous sample, use of catalyst or not).

The temperatures corresponding to the cumulative combustion of 25, 50 and 75 wt% of the total carbon-based material put in the sample holder (temperatures that for each kind of sample changes with the heating rate) have been used to calculate the activation energy according to the Ozawa method [28, 29].

According to this method, each DTA pattern provides the temperature  $(T_{\alpha,i})$  at which a " $\alpha$ " fixed fraction of carbon (for instance  $\alpha = 0,5$ ) is burned during the DTA run carried out with the heating rate  $\phi_i$ . In such a way, with reference to every specific kind of sample (type of carbon, kind of catalyst if it is present) and of  $\alpha$ , a set of couples of ralated values of  $T_{\alpha,i}$  and  $\phi_i$  were obtained. These values were found to fulfil the linear equation proposed by Ozawa:

 $ln(\phi_i)=B-0,4567(Ea/R T_{\alpha,i})$ 

where:

(4)

B is a constant, whose value depends on the pre-exponential factor in the Arrhenius equation as well as on the fixed fraction of burned carbon at which  $T_{\alpha,i}$  is taken;

E<sub>a</sub> is the activation energy for the combustion reaction under investigation;

R is the constant of ideal gas law.

The linear plot that best fits each experimental data serie of  $ln(\phi_i)$  versus  $1/T_{\alpha,i}$  can be drawn; form the slope of this plot the activation energy was calculated according to eqn. (4).

## Temperature programmed desorption of oxygen

The capability of ceria to act as an oxygen pump was investigated by temperatureprogrammed-desorption (TPD) of oxygen, carried out in a Termoquest TPD/R/O 1100 analyzer, equipped with a thermal conductivity detector (TCD). A fixed bed of catalyst was enclosed in a quartz tube and sandwiched between two quartz layers; then an oxydation pre-treatment was carried out. To this purpose the catalyst was heated under an oxygen flow (40 Nml/min) up to 750°C then, after a 30min stay at this temperature under O<sub>2</sub> flow, the reactor temperature was lowered down to room temperature under oxidizing atmosphere, thereby inducing complete oxygen adsorption over the catalyst.

Afterwards, He has been fed to the reactor at a 10 Nml/min flow rate for one hour at room temperature, thereby eliminating any excess of gaseous oxygen.

The temperature programmed desorption test was performed by heating the catalyst up to 1100°C at a 10°C/min rate under helium flow. The oxygen desorbed during heating was detected in the outlet flow by a TCD detector.

## Catalyst ageing procedure

The possible detrimental effect caused by prolonged high temperature operation on the catalytic activity of ceria was investigated, as well as the poisoning effect caused by some components of diesel exhausts (e.g.  $SO_2$ ,  $H_2O$ ). In line with earlier investigations on other soot-combustion catalysts [30], in order to consider separately the effect of each of these factors, aging treatments were performed under the following conditions:

- thermal ageing in dry air at 600°C for 96h;
- thermal ageing at the same temperature and time values under wet air, containing 12 vol% of moisture obtained by humidification in thermostasized bubble column;
- thermal ageing at the same temperature in air containing 1000 ppmv SO<sub>2</sub>, a value much larger than current SO<sub>2</sub> levels in exhaust gases (a few ppms), fixed for the sake of accelerating the possible effect of this specific poison.

All these treatments were carried out in a tubular furnace under a gas flow of 100 Nml/min.

Most of the physical and chemical characterisation analyses described above were replicated on aged samples.

# **Results and discussion**

#### Catalyst characterization

The catalyst prepared by combustion synthesis showed the same crystalline structure of the ceria obtained by decomposition of the nitrate; the XRD diffraction patterns belonging to these materials are compared in Figure 1. Only diffraction peaks characteristic of ceria are present in both XRD spectra, thus showing that any secondary phases did not form during each of used methods. The degree of crystallization of both samples is equivalent, as the peak absolute and relative intensities as well as peak widths in the two spectra are quite close.



**Fig. 1.** XRD diffraction patterns of the CeO<sub>2</sub> catalysts: A) ceria prepared by combustion synthesis, B) ceria prepared by thermal decomposition (markers are located according to the PDF 34-0394 CeO<sub>2</sub> card).

Figure 2 shows the morphology of ceria achieved by solution combustion synthesis (fig. 2a) and that of the catalyst obtained by thermal decomposition (fig. 2b) respectively. In both cases ceria particles are agglomerated but the morphology of such agglomerates seems quite different. In particular, combustion synthesis gives rise to a finely-divided spongy structure made of aggregates of irregular shape, each made of very small particles. The porosity of this material is due to the large amount of gaseous species emitted during the synthesis. The bonds between the particles in this foamy structure appears to be weaker and the sponge can thus be very easily crumbled, thereby giving rise to small distinct particle aggregates.

The ceria prepared via nitrate decomposition seems to have a more coarse structure, despite the same specific surface area ( $60 \text{ m}^2/\text{g}$ ). The pore size distribution evaluated from N<sub>2</sub> desorption isotherms (Fig. 3) fully confirms this impression. The SCS-synthesized ceria is characterized by a rather monomodal pore size distribution in the range 5-15 nm, i.e. the same order of magnitude of the size of the single ceria crystals prepared by this method. The absence of much finer pores suggests that the crystal are

non porous and that the surface area exposed by this material is substantially equal to the geometrical surface area exposed by these crystals. Conversely, the pore structure of the ceria obtained by nitrate decomposition is multimodal with peaks at about 60, 15 and 2 nm. This rather complex pore structure may hamper the direct contact of soot with the entire specific surface area exposed. As opposed to gaseous molecules, soot particles are too large to get inside complex pore structures.



**Fig. 2.** Microstructures of  $CeO_2$  prepared by two different methods: a. by solution combustion synthesis. b. by nitrate thermal decomposition.



Fig. 3. Pore size distribution of the two ceria materials prepared: solid line = SCS ceria; dashed line = ND ceria).

#### Catalyst activity

Figure 4 compares the TPC plots obtained with the Ceria samples obtained by SCS and nitrate decomposition (ND) as well as that of non-catalytic combustion of Printex U. The peak combustion temperatures deduced by the TPC plots were also reported in Table 1 for a more reliable comparison. The activity order is clearly SCS-CeO<sub>2</sub> > ND-CeO<sub>2</sub> > non catalytic combustion. Both catalysts clearly display under tight contact conditions a significant catalytic activity. However, the SCS-CeO<sub>2</sub> does definitely induce a faster combustion of the carbon-black which occurs at comparatively lower temperatures. This occurs also in the case of diesel soot combustion (Figure 5). As expected, soot combustion occurs at a lower temperatures that that of PrintexU for both the catalytic and non catalytic cases, owing to the higher level amount of hydrocarbons adsorbed on the soot particle surface which makes ignition easier [21]. The difference in the SCS and ND prepared ceria seems here even more remarkable.



**Fig. 4.** TPC of PrintexU performed with both CeO<sub>2</sub> from combustion synthesis (SCS-CeO<sub>2</sub>) and thermal decomposition (ND-CeO<sub>2</sub>); the direct, non-catalytic carbon-black combustion is also depicted for comparison. Solid line: tight contact conditions; dashed line: loose contact conditions.

The activity of the best-performing catalysts (SCS-CeO<sub>2</sub>) under loose-contact conditions is somehow reduced, as expected. However, this decrease is not severe. The loose-contact activity of the SCS-synthesized ceria remains comparable or even better (diesel soot case) than the tight-contact activity of ND-CeO<sub>2</sub>, despite the higher number of contact points between catalyst and soot enabled by the tight-contact conditions.

Two reasons might explain the different behaviors noticed:

1) the microstructure of SCS-CeO<sub>2</sub> is intrinsically more suitable to achieve a high number of contact points with the carbonaceous counter part owing to the above mentioned pore micro-structure;

2) the nature, amount or spill-over aptitude of the oxygen species delivered by the SCS-CeO<sub>2</sub> towards the soot is higher than that of the nitrate-derived one.



**Fig. 5.** TPC of diesel soot performed with both  $CeO_2$  from combustion synthesis (SCS-CeO<sub>2</sub>) and thermal decomposition (ND-CeO<sub>2</sub>); non-catalytic diesel soot combustion is also reported for comparison. Solid line: tight contact conditions; dashed line: loose contact conditions.

As for the point 1 above, the earlier examined FESEM pictures of the two compared materials

<b>Combustion reaction</b>	Ea [kJ/mol]		
Soot	149		
$Soot + CeO_2 scs$	111		
Soot + $CeO_2$ nitrate	115		
Printex U	154		
Printex $U + CeO_2 scs$	114		
$PrintexU + CeO_2$ nitrate	121		

**Table 1.** Activation energy values for PrintexU and soot combustion

 calculated by the Ozawa method on the basis of DTA results

strengthen this hypothesis. The SCS-synthesized material clearly exposes a much rougher geometrical surface which plays in favor of an increase of the number of contact points with soot particles which have dimensions comparable with those of the single crystals of the catalyst aggregates.

Conversely, in order to draw conclusions concerning point 2 above, activation energy and TPD/TPR experiments had to be performed.

The activation energy values, calculated by processing the differential thermal analysis data according to Ozawa method (Figure 6 a particular set of Ozawa plots as an example), are listed in Table 1.

The activation energy for not-catalysed combustion of PrintexU is only slightly higher than that of soot. However, the calculated activation energy value has to be regarded as the average value of activation energies for different reactions: the main reaction of carbon combustion and the secondary reactions of combustion of each kind of hydrocarbon adsorbed on the surface of the carbon particle aggregates.

The activation energy was lowered when using both ND and SCS ceria. The adoption of the latter catalyst was more effective and decreased the activation energy somehow more than the former for both soot and Printex U combustion. As the number of contact points should play no significant role



**Fig. 6.** Ozawa plots related to soot combustion catalyzed by  $CeO_2$  obtained by combustion synthesis allowing for the evaluation of the activation energy (E<sub>a</sub>) at different levels of carbon conversion ( $\alpha$ )

on the activations energy, this occurrence should play in favour of considering the oxygen species delivered by the SCS-CeO<sub>2</sub> catalyst as more active than those delivered by the ND-CeO<sub>2</sub>. However, differences are perhaps too limited to draw final conclusions to these merits.

#### **TPD** experiments

Many oxidation catalysts are known to act as an oxygen pump, owing to the capability of absorbing oxygen on their surface and releasing it, when they are put in contact with a reducing agent, or the capability of changing the oxygen content in their crystalline lattice in combination with changes in the valence of transition metals. A noticeable example of oxidation catalyst acting as an oxygen pump is LaCrO<sub>3</sub>, which recently was proved to be quite effective in carbon combustion, as well as other similar perovskites [31-33].

With the aim of investigating the occurrence of such a mechanism on the two types of ceria synthesized, temperature adsorption and reduction experiments were performed.

Figure 7 shows that SCS-ceria releases most oxygen in the temperatures range between 400 and 600°C. It is very likely that reaction with the carbonaceous materials (diesel soot of Printex U) can anticipate the release of the above oxygen even at lower temperatures. Carbon starts indeed burning in the presence of the SCS-ceria at or even below 300°C (Figures 4 and 5). When the reaction is in progress, the oxygen lost by ceria for carbon combustion is routinely replaced by oxygen coming from the gaseous atmosphere, thus giving rise to a loop for oxygen transfer.

Figure 7 shows that the nitrate-derived ceria does release oxygen but in a lower amount and at temperatures higher than its SCS-synthesized counter part. The lower activity of the ND catalyst in the TPC tests should be in direct connection to this behavior.

A closer look to the TPD plots suggests the existence of two oxygen desorption patterns: the first related to weakly chemisorbed suprafacial oxygen desorbed below 600°C, the second related to more strongly chemisorbed or even bulk oxygen. The most striking difference between the two ceria samples lies in the first of these oxygen species whose presence is maximized in the case of the more active SCS-CeO<sub>2</sub>.



**Fig. 7.** Results of the oxygen TPD tests on  $CeO_2$  from combustion synthesis (SCS-CeO<sub>2</sub>) and  $CeO_2$  from nitrate thermal decomposition (ND-CeO<sub>2</sub>).

## Catalyst durability

An important characteristic required to these catalysts for exploiting their potential in devices for abatement of pollutants emitted by terrestrial vehicles is the capability to keep their catalytic

T <sub>p</sub> [°C]	fres h	96h- 600 °C dry	96h- 600 °C wet	96h- 600 °C SO <sub>2</sub>
no catalyst-printexU	560	-	-	-
CeO <sub>2</sub> scs	405	439	445	441
CeO <sub>2</sub> nitrate	466	528	531	530

**Table 2.** TPC peak temperatures (°C) before and after different ageing treatments (runs performed at 5°C/min using Printex U as carbonaceous material)

Table 3. BET values of catalysts before and after ageing

BET [m <sup>2</sup> /g]	fresh	96h-600 °C dry	96h-600 °C wet	96h-600 °C SO <sub>2</sub>
CeO <sub>2</sub> scs	60	52	50	48
CeO <sub>2</sub> nitrate	60	39	36	30

activity preserved after operation at high temperature or in the presence of poisoning substances. For this reason, both nitrate and combustion synthesized ceria were submitted under specific aging protocols. As far as the activity of ceria by solution combustion synthesis is concerned, no serious deactivation was found after any of the tested ageing protocols. The highest deactivation (limited, however, to an increase of about 40°C of the  $T_p$  value; Table 2) was noticed for the hydrothermal ageing, which mostly affected the specific surface area of the catalyst (Table 3).



**Fig. 8.** Microstructure of  $CeO_2$  prepared by solution combustion synthesis after ageing at 600°C for 96 h in SO<sub>2</sub>.

Conversely, in the case of the ceria produced by thermal decomposition, the deactivation is more severe (Table 2) as a consequence of a more significant drop of the specific surface area values (Table 3). A possible explanation lies in the fact that the preparation of the ND-CeO<sub>2</sub> occurs at 600 °C while the solution combustion synthesis method is a route in which the prepared materials reach a temperature higher than 1000 °C [26], even if for a very few seconds. As a consequence, prolonged treatment at 600°C is likely to let the microporous structure of the ND-ceria evolve towards lower specific surface areas than the SCS material. Moreover, the nano-cristalline structure of the SCS-ceria, at least in part preserved after prolonged hydrothermal treatment as shown in the FESEM picture in Figure 8, should indeed hinder the sintering phenomena.

EDAX analysis on FESEM samples of the catalysts aged in  $SO_2$  laden atmosphere put into evidence the presence of sulphate species on both the catalysts tested. However, these species did not significantly affect the activity of the catalysts compared to that of the catalysts aged in the absence of  $SO_2$ .

## Conclusions

Ceria powders obtained by solution combustion synthesis show high catalytic activity in the combustion of carbonaceous materials, including diesel soot. This catalyst can lower greatly both the ignition temperature and the activation energy for carbon combustion.

The activity of this material was found to be related to its microstructure, which favors intensification catalyst-soot contact points, as well as to exchange oxygen with the atmosphere and/or carbon through surface oxidation/reduction phenomena at temperatures below 600°C.

Furthermore, ceria produced by combustion synthesis shows good thermal stability and, after exposition to high temperature, it keeps a rather large surface area and good catalytic activity, as a likely consequence of the irregular shape of ceria particles and crystal aggregates, which hinder sintering phenomena.

#### References

- 1. P. Denis, J. Lemarie, O. Toret, U.S. patent 6 093 223 (2000).
- 2. M. O'Connel, M.A. Corris, Catal. Today, 59 (2000) 387.
- 3. B. Krutzsch, G. Wenninger, SAE Technical Series, 922188, (1992).
- 4. Y. Teraoka, S. Kagawa, K. Nakano, W.F. Shangguan, Catal. Today, 27 (1996) 107.
- 5. W.F.Shangguan, Y.Teraoka, S.Kagawa, Appl. Catal. B: Environmental, 8 (1996) 217.
- 6. D.W. McKee, Carbon, 8 (1970) 623.
- 7. D.W. McKee, Carbon, 8 (1970) 131.
- 8. A.F. Ahlstrom and C.U.I. Odenbrand, Appl. Catal. B, 60 (1990) 151.
- 9. D.W. McKee and D. Chatterij, Carbon, 13 (1975) 381.
- 10. M.L. Pisarello, V. Milt, M.A. Peralta, C.A. Querini, E.E. Miro, Catal. Today, 75 (2002) 465.
- 11. W.F. Shangguan, Y. Teraoka, S. Kagawa, Appl. Catal. B: Environmental, 8 (1998) 149.
- 12 Y. Watabe, K. Yrako, T. Miyaijma, T. Yoshimoto, Y. Murakami, SAE paper 830082 (1983).
- 13. P. Ciambelli, M. D'Amore, V. Palma, S. Vaccaro, Comb. and Flame, 99 (1994) 413.
- 14. G. Mul, J.P.A. Neeft, F. Kapteijn, M. Makkee, J.A. Moulijn, Appl. Catal. B, 6 (1995) 339.
- 15. C. Badini, G. Saracco, V. Serra, Appl. Catal. B, 11 (1997) 307
- 16. D. Fino, N. Russo, C. Badini, G. Saracco, V. Specchia, AiChE Journal, 49 (2003) 2173.

- 17. R.E. Mariangeli, E.H. Homier and F.S. Molinaro, in: Catalysis and Automotive Pollution Control, Elsevier, Amsterdam, 1987, p. 457.
- 18. J. Van den Tillaart, L. Leyrer, S. Eckhoff, E.S. Lox, Appl. Catal.B, 10 (1996) 53.
- 19. M. Boaro, M. Vicario, C. de Leitenburg, G. Dolcetti, A. Trovarelli, Catalysis Today, 77 (2003) 407-417.
- 20. J.P.A. Neeft, M. Makkee, J.A. Moulijn, Appl. Catal. B, 8 (1996) 57.
- 21. B.A.A.L. van Setten, M. Makkee, J.A. Moulijn, Catal. Rev. Sci. Eng. 43 (2001) 489.
- 22. K.C. Patil, S.T. Aruna, S. Ekamaram, Current opinion in Solid State and Material Science, 2 (1997) 158.
- 23. K.C. Patil, S.T. Aruna, T. Minami, Current opinion in Solid State and Material Science, 6 (1997) 507.
- 24. M.M.A. Sekar, S.S. Manoharan, K.C. Patil, J. Mater. Sci. Lett., 9 (1990) 1205.
- 25. C. Badini, P. Fino, M. Pavese, S. Biamino, G. Saracco, Patent Application TO2005A000080 (2005).
- 26. A. Civera, M. Pavese, G. Saracco, V. Specchia, Catal. Today, 83 (2003) 199.
- 27. J. P. A Neeft, M. Makkee, J.A. Moulijn, Fuel, 77 (1998) 111.
- 28. T. Ozawa, J. Therm. Anal., 2 (1970) 57.
- 29. T. Ozawa, J. Therm. Anal., 7 (1975) 301.
- 30. Cauda E., Mescia D., Fino D., Saracco G., Specchia V., Ind. Eng. Chem. Res., 44 (2005) 9549.
- 31. D. Fino, V. Specchia, Chem. Eng. Sci., 59 (2004) 4825.
- 32. D. Fino, N. Russo, G. Saracco, V. Specchia, J. of Catalysis, 217 (2003) 367.
- 33. N. Russo, D. Fino, G. Saracco, V. Specchia, J. of Catalysis, 229 (2005) 459.