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Evaluation of sol-gel methods for the synthesis of doped-ceria environmental catalysis systems. Part I: preparation of coatings

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Abstract

Sol-gel technology can be employed for the synthesis of multi-component nanophase environmental catalysts with enhanced catalytic activity, controlled composition and tailor-made pore structure together with their simultaneous deposition upon porous supports. The conditions for effective deposition of nano-phase doped-ceria systems onto cordierite honeycombs through sol-gel routes were investigated. For the direct casting from the sol phase, the sol rheological characteristics were adjusted and optimized so that homogeneous smooth washcoats were obtained. In this way, integrated support-catalyst assemblies suitable for high-temperature gas-solid catalysis were prepared. To overcome the inherently low loading percentage achieved per impregnation when depositing directly the sols, the synthesis of sol-gel powders and their deposition from aqueous slurries, as well as hybrid deposition methods using sol-gel powders dispersed in sols were tested as alternatives. The hybrid sol/powder systems proved to be the most attractive by combining an effective loading procedure with desirable and fine-tuned coating characteristics. © 2001 Elsevier Science Ltd. All rights reserved.

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1. Introduction

Ceria has found extensive use in three-way automobile catalysts (TWC) because of its ability to act as an oxygen storage agent.[1–5] It is by now well established that nanophase ceria materials themselves can also exhibit catalytic activity for reactions such as the reduction of nitrogen oxides by carbon monoxide,[6,7] oxidation of volatile organic compounds (VOCs)[8,9] as well as carbon monoxide oxidation.[10–12] The catalytic activity of ceria can be further enhanced by partial substitution (doping) of cerium atoms in the cerium oxide lattice by other metal atoms of a lower oxidation state, such as Ca^{2+} or Nd^{3+}.[13] These findings can be exploited to drastically reduce the amount of expensive noble metals required for effective three-way catalysis. Soft chemistry synthesis methods such as co-precipitation and sol-gel are prime candidates for the preparation of such systems, since they allow the synthesis of highly active, nanophase materials with precise tailoring of both catalyst composition (doping) and microstructure.[14–20] Sol-gel synthesis in particular, has the additional inherent advantage of allowing the production of materials directly cast upon substrates. Supported thin films and membranes can then be easily produced in one step during firing treatment, by the simultaneous formation of the desired ceramic phase and its adhesion to the substrate.

For the actual operation of high-temperature exhaust gas catalytic applications, the configuration of choice is the multi-channeled honeycomb substrate (monolith) that permits a high gas flow rate under low pressure drop. Because of thermal shock resistance requirements, these honeycombs are usually made of cordierite (a ceramic

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material with very low thermal expansion coefficient) and are characterized by porosity of about 30%, mean pore diameters in the range 5–20 μm and a negligible specific surface area. These pore dimensions are significantly higher than the colloidal dimensions of sol particles. When a sol is used for coating the walls of a cordierite honeycomb, it can very easily penetrate and gel into the honeycomb pores. This infiltrated material becomes "wasted" since it is not readily accessible to the gaseous reactants — a fact that can adversely affect the cost since the sol may also contain the precious metal precursors.

Many studies have appeared recently in the literature concerning the sol-gel synthesis of doped-ceria powders and their characterization with respect to oxygen storage capacity and catalytic activity; these are reviewed in part II of this work.[20] Many of these studies involve the preparation of high surface area powders by heat-treatment of a sol in the range 500–700°C. These sol-gel derived powders are then dispersed in slurries which are used to coat the honeycomb channel walls. The resulting washcoat is often referred to as 'sol-gel derived' although the sol is not directly used to cast the catalytic ceria-based coating. A number of studies on the catalytic performance of such elements has been reported in the patent literature.[21–23] From a general point of view, very little information and limited patent literature,[24–27] exist on the direct deposition of sols on porous honeycomb supports, although the direct deposition of sols on tubular or flat porous supports is widely used (even industrially) for the synthesis of ceramic membranes.[28–31] This gap could be attributed to the large pore sizes of commercial cordierite honeycombs that are not favorable for the deposition of homogeneous, surface coating from sols. In order to avoid sol penetration in honeycombs, a number of methods have been suggested in the literature. A preliminary filling of the honeycomb pores with water is the first example:[26,27] when the alkoxide sol is deposited on the channel walls, it contacts the water already occluded in the pores and converts to a gel which remains on the surface.[26] Another approach consists of causing the gelation of the deposited sol by flowing ammonia[24] or steam;[26] however, no evidence is provided (such as micrographs) that gelation occurs only on the channel walls and not inside the porous structure. Direct coating of honeycombs with alumina sols has been reported[25] but no adjustment of the sol viscosity is mentioned and the very thin coating obtained suggests that a significant amount of the sol has penetrated inside the support porous structure. Recent articles[32] and patents[33–35] report the coating of honeycombs with a combination of milled powder slurries and sols. Researchers of the Toyota group have employed a first impregnation with a mixture of alumina powder and alumina sol, followed by post-impregnation of the precious metals and an oxygen storage component (Ba).[33] Alternatively, the preparation of a doped-alumina sol-gel made powder, post-impregnation with Pt and subsequent mixing with an alumina[34] or a zirconia sol[35] to form the coating medium, was also suggested by the same authors.

In a previous work by some of the present authors[36,37] the synthesis of doped nanophase ceria via sol-gel methods was extensively investigated. Both organic and inorganic precursors were employed and the synthesis of a wide range of compositions was achieved. Through oxygen storage capacity and catalytic activity measurements on catalyst powders, an optimal washcoat composition based on doping with calcia and containing small amounts of Pd and Rh was identified. The present work is concerned with the effective deposition of this catalyst/carrier system upon ceramic honeycombs whereas a second part[20] deals with the catalytic testing of the integrated support/catalyst assembly. Preliminary results on the deposition of nanophase ceria systems on ceramic honeycombs directly from the sol have been already reported[38] — the present study further addresses the problems identified in the deposition process.

2. Experimental

The sols and respective powders employed in this study were synthesized via two sol-gel routes: from metallo-organic (polymeric route) and inorganic (colloidal route) precursors. The proportions of the precursors (salts or metallo-organic compounds) were selected such as to lead to the required final stoichiometry: $(CeO)_{0.25}(CaO)_{0.02}(Al_2O_3)_{0.73}$. The reasons for choosing this composition as well as the details of the synthesis routes have been reported elsewhere.[36,37] For the colloidal route, boehmite, cerium and calcium chlorides were employed as precursors for preparing the aqueous sol, whereas the polymeric sol was prepared in hexylene glycol by using $Ce(acac)_3.H_2O$, $Ca(OMe)_2$ and aluminum butoxide as precursors. In some cases (specifically mentioned in the next sections) noble metal precursors were directly inserted at the sol stage. In these cases, the Pd and Rh contents in the final washcoat were finely tuned and fixed respectively to 1.36 wt.% and 0.14 wt.%. In the other cases, noble metals were inserted after deposition and heat-treatment of the washcoat, by classical post-impregnation with salts.

Cylindrical cordierite specimens manufactured by Ceramics and Refractories Technological Development Company (CERECO), Greece, with 400 square cells/in^2 (diameter 1.5 cm; length 2 cm; porosity 32%, mean pore diameter = 10 μm) were used as supports. These characteristics are typical for honeycombs used in automotive exhaust systems. Details of manufacturing of the honeycombs as well as of the tuning of the porosity and of the pore size distribution have been reported elsewhere.[39]

Sol viscosity was adjusted with the addition of various binders and with sol concentration by mild evaporation at 70°C under vacuum, and measured with a rotating-spindle viscometer (Brookfield RVT DV- II). For coating the supports directly from sols, honeycomb specimens were dived in the optimized sol under stirring. In order to improve the coating process, parameters such as precursor concentration, pH, organic binders (type and quantity), contact time sol/support (30 min to 4 h) and drying conditions (temperature, atmosphere) were extensively studied. The loaded specimens were withdrawn from the sol and excess liquid was removed by blowing air through the honeycomb channels. Then the specimens were dried at 100°C and finally heat-treated at 700 or 1000°C in air for 2 h. Drying and subsequent firing treatments lead to the formation of a calcia-doped-ceria layer covering the honeycomb channel walls.

Alternatively, suspensions prepared with powders derived from the sols mentioned above have also been used for deposition. These powders were obtained by drying the sol at 60°C for 1 h under vacuum and subsequent calcination for 2 h at 450 or 700°C. In this way, calcia-doped-ceria nanophase, but aggregated, powders were obtained. The powders were then ball-milled (aqueous slurry, alumina grinding media) in order to reduce the size of the agglomerates produced during heat-treatment. Aqueous slurries of the ball-milled powders were prepared, with optimized rheological characteristics (viscosity, stability) via addition of proper dispersants and tuning of the solids content in the slurry. Honeycomb impregnation, removal of excess slurry, drying and subsequent firing treatment took place by the procedure described above.

Finally, a specific quantity of a sol-gel-derived powder was added in a particular sol under stirring to form hybrid sol-powder systems. The quantity of powder in the sol was varied from 1 to 30 wt.%. After homogenization of the mixture, monoliths were impregnated using the same procedure as described above. A schematic of the three routes employed for the washcoating of monoliths is shown in Fig. 1.

For each of the honeycomb loading experiments, five specimens were prepared in order to check for reproducibility of the coating procedure, as well as to prepare enough samples for the subsequent characterization experiments. The effectiveness of each coating process was evaluated from the loading percentage achieved per impregnation (determined from the weight increase of the honeycomb after the firing treatment) as well as from observations of the washcoat morphology (thickness, homogeneity, adhesion and microstructure) with the aid of scanning electron microscopy (Jeol JSM-6300 and LEICA Stereoscan S260). The coated honeycombs were

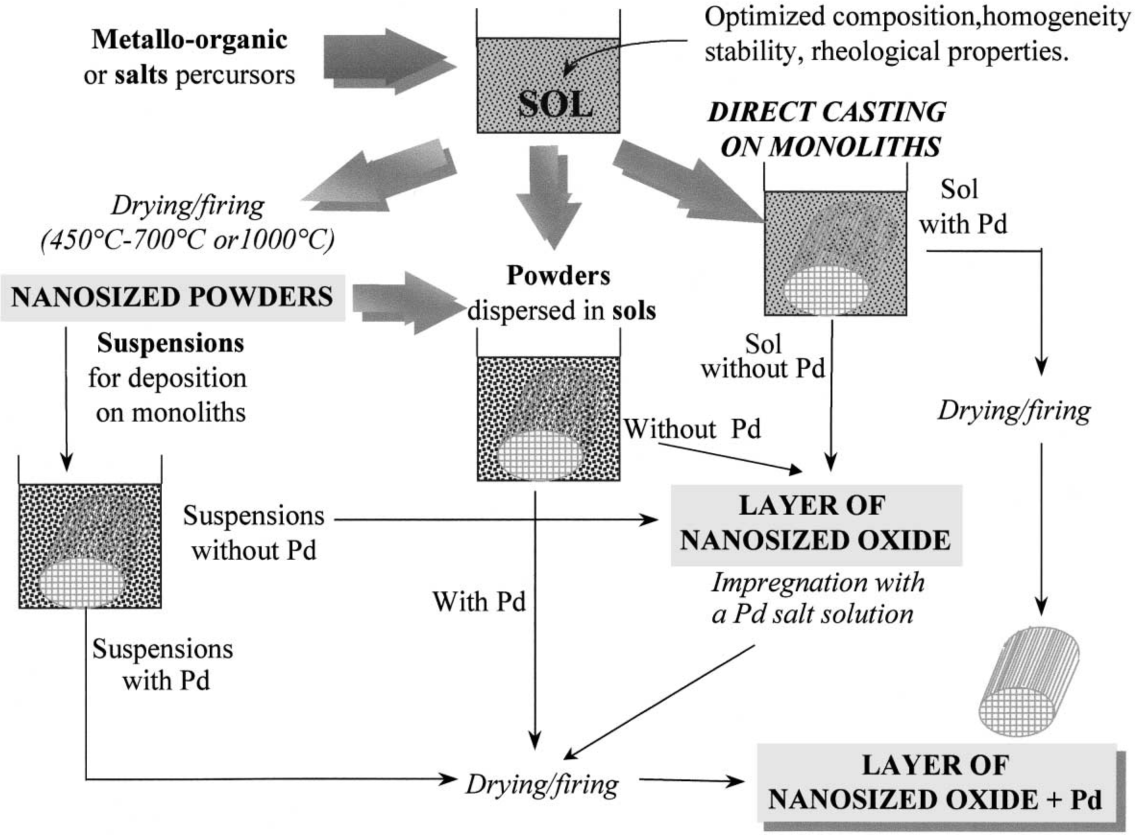


Fig. 1. Schematic of the deposition routes followed.

characterized with respect to specific surface area and pore size distribution with the aid of nitrogen adsorption–desorption (Micromeritics ASAP 2000) and mercury porosimetry (Quantachrome Autoscan 500 porosimeter). Comparative characterizations with respect to resistance to thermal aging and catalytic activity are the subject of the second part of the work. [20]

3. Results and discussion

3.1. Washcoating of honeycombs

3.1.1. Washcoating directly from the sols

As previously mentioned, an inherent advantage of sol-gel methods is that they can be potentially employed for casting washcoat layers upon porous supports directly from the liquid phase. However, direct impregnation of honeycombs with the as-prepared sols induces particular problems that have to do with the high solvent content in the sol. The problem of sol penetration already discussed, is exemplified in Fig. 2 where a single honeycomb channel wall loaded with an inorganic ceria/boehmite sol without any binder addition is shown. It can be clearly observed that the channel wall is not at all covered with the washcoat layer: instead, the sol has penetrated and gelled into the pores of the cordierite support, which have become either completely or partially filled with a gel-like layer.

Another problem linked to the direct deposition from sols, is the very low loading values achieved per impregnation. Since the starting sols contain a large amount of solvent that evaporates during drying and firing, the amount of oxide phase that actually remains on the honeycombs after these steps is very low (about 0.5 wt.%). Thus, a large number of successive impregnations (followed by the respective drying and firing steps) is required for the honeycomb to be loaded with an adequate quantity of washcoat.

In order to solve these problems, methods that could increase the sol viscosity as well as the precursors concentration were investigated : sol concentration by evaporation and addition of organic binders (of various types and quantities). In preliminary screening experiments, the performance of several types of binders has been compared, in terms of viscosity control and ease of removal during the firing step without causing extensive defects to the gel layer. It occurred that poly-vinyl-alcohol (PVA — Erkol 23/88, Rhodia) was the most suitable for the inorganic sols, although poly-vinyl-butyral (PVB — Aldrich) was more adapted to the organic ones. However, the sole addition of a binder in the sol, even up to high proportions (20 wt.% in the sol) was not efficient enough for both eliminating the infiltration phenomenon and increasing sufficiently the loading percentage. Further increase in binder concentration increased only marginally the sol viscosity but affected adversely the washcoat integrity by increasing shrinkage and formation of defects.

Further adjustment of sol viscosity was achieved for the aqueous sols by solvent evaporation at 70°C under vacuum. The loadings achieved as a function of sol concentration, for two inorganic sols with and without boehmite and for the same PVA binder content of 20 wt.%, are shown in Fig. 3. For practical purposes, there exists an upper limit for sol concentration: beyond a certain point, sol viscosity increases significantly yielding a very viscous liquid which sometimes cannot even penetrate inside the honeycomb channels, and certainly cannot be uniformily deposited on the honeycomb channel walls. For inorganic sols this upper limit for sol concentration was about 20 wt.% of the initial sol weight. The concentration step increased the sol viscosity, reduced the sol infiltration in the support and

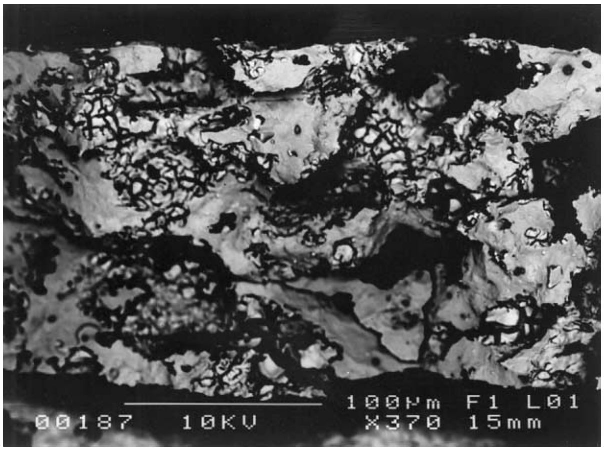


Fig. 2. Loading directly from sols (magnification of a single channel wall) where penetration of the sol into the support pores due to low sol viscosity can be seen.

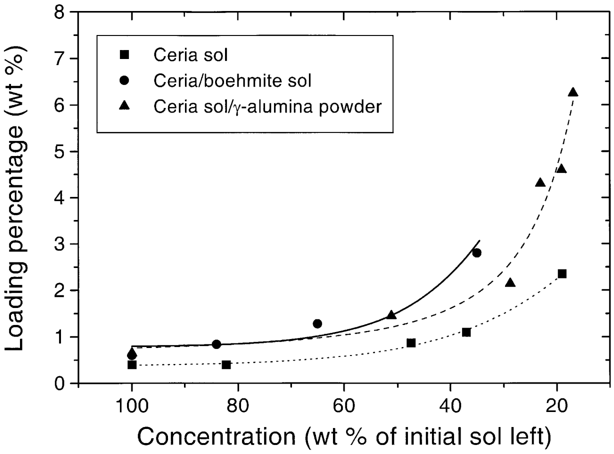
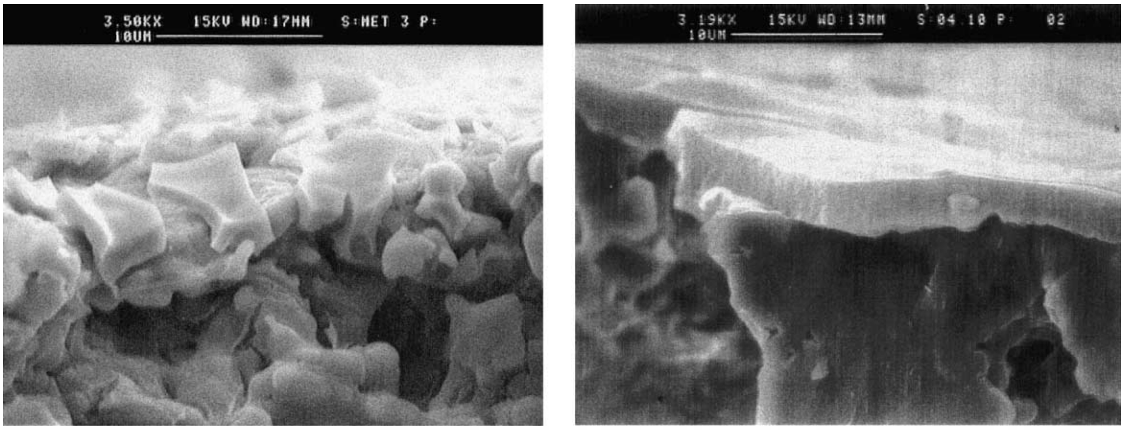


Fig. 3. Effect of sol concentration on loading percentage (inorganic sol) for the cases of deposition directly from the sol and through hybrid (ceria sol)/(γ-alumina powder) systems.

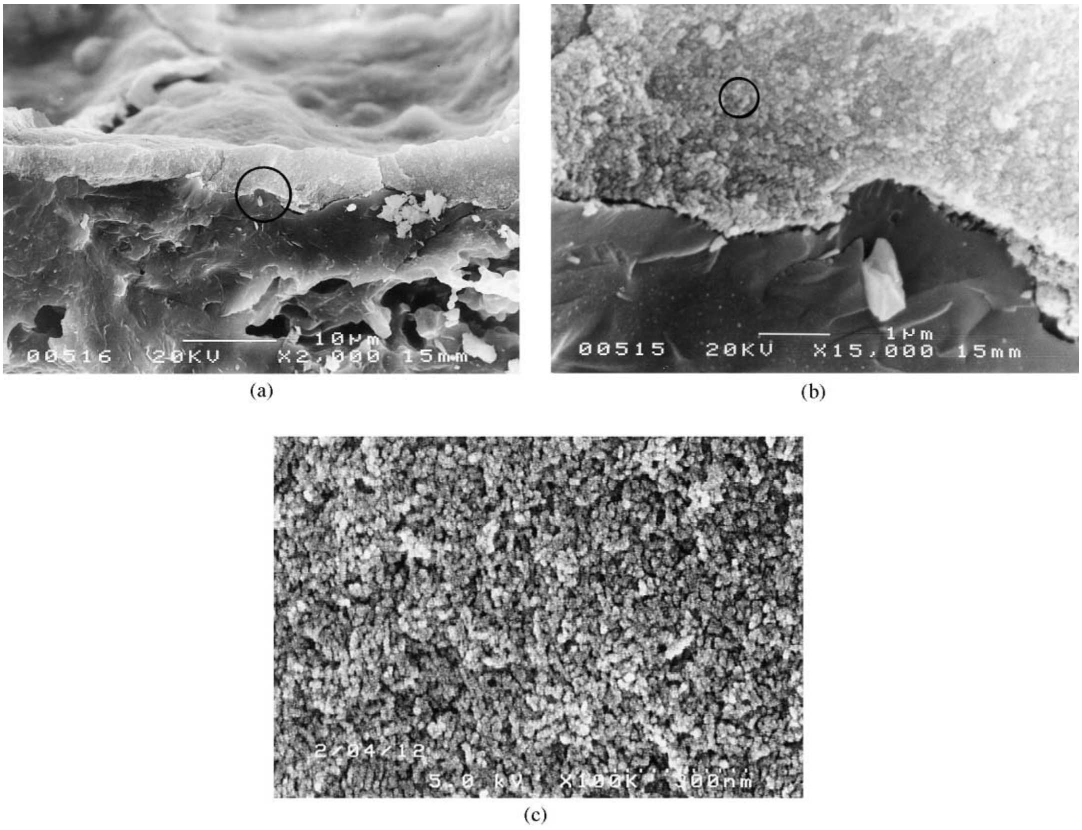
improved the loading percentage achieved per impregnation. However, it can be seen that significant sol concentration (above 50%) is required for loading percentage to exceed 1 wt.%; even with the most viscous sol, loading could not exceed 3.0 wt.% per impregnation.

Such a concentration step was not possible for organic sols that tend to gel readily after synthesis. With an optimal combination of conditions (support characteristics, sol composition, quantity of PVB, sol/support contact time, drying/firing conditions) the direct casting of these homogeneous sols on honeycombs could lead to surface washcoat layers. More specifically, when the honeycombs were impregnated with the sol for 30 min under vacuum and then dried in humid atmosphere, ultra-thin cracked layers, fairly adhering to the support, were obtained (Fig. 4a). In comparison, the sol viscosity/deposition/gelation was much more easily controlled in the case of inorganic aqueous sols, the



(a) (b)

Fig. 4. SEM observations of $(CeO)_{0.25}(CaO)_{0.02}(Al_2O_3)_{0.73}$ layers deposited on cordierite honeycomb supports from (a) organic and (b) inorganic precursor sols, calcined in air at 1000°C for 2 h.



(a) (b)

(c)

Fig. 5. Loading with concentrated inorganic sol: (a) support/washcoat interface at a magnification of 2000 times, (b) support/washcoat interface (region marked in Fig. 5a) at a magnification of 15000 times, (c) washcoat particles (region marked in Fig. 5b) at a magnification of 100,000 times.

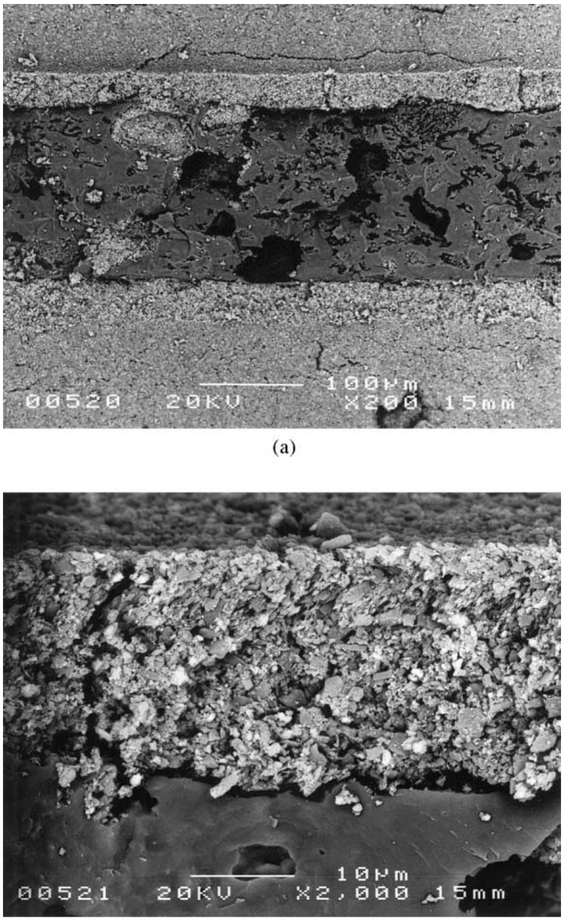
gelation of which was more gradual. As a consequence, more homogeneous and reproducible deposits could be obtained with inorganic (colloidal) sols, even without any specific sol concentration step (Fig. 4b). The much higher quality of the washcoat derived from the inorganic sol (much fewer cracks) fits with the thermal expansion studies performed on the powders derived from both inorganic and metallo-organic precursors.[36] However, it can be observed in Fig. 4 that the thickness of the deposited layers is limited to less than 2 μm with a single impregnation. Typical honeycomb loadings were about 5 wt.% for the organic and 2 wt.% for the aqueous sols (Fig. 4a and b, respectively) revealing a higher extent of sol infiltration in the first case.

Multiple impregnations with concentrated colloidal sols were then tested for loading honeycombs with a sufficient amount of washcoat (i.e. ~10 wt.%) covering the channel walls. Fig. 5. shows the morphological details of a honeycomb impregnated six times with a concentrated ceria/calcia/boehmite inorganic sol and heat-treated at 700°C (total loading 7.5 wt.%). It is clear from the micrograph of the support/washcoat interface shown (Fig. 5a) that the high sol viscosity completely prevented the sol infiltration into the support pores: a smooth washcoat layer about 5 μm thick has been formed on the external channel surface. The enlargement of the support/washcoat interface (Fig. 5b) reveals the good adhesion of the washcoat on the support and the very fine and homogeneous texture of the ceramic layer. Finally, a very high magnification (Fig. 5c) demonstrates the tight packing of the washcoat particles and their nano-structure (size is about 20 nm).

To summarize, even when the rheological properties of a sol can be adjusted in order to prevent sol infiltration into the honeycomb pores, the direct deposition from sols leads to ultra-thin layers ($\leqslant 2$ μm per impregnation), often heterogeneous and sometimes unable to cover the whole channel surface (especially in the case of organic sols). Multiple impregnations are required in order to load honeycombs with an adequate amount of washcoat covering homogeneously the channel walls. By this route, thin, compact layers, very strongly adhered on the support can be obtained (Figs. 4 and 5).

3.1.2. *Washcoating with sol-gel derived powders*

An alternative approach to overcome the problem of low loading achieved per impregnation when depositing directly from sols, is to synthesize powders from the sols and to use these nanophase powders to prepare aqueous slurries adapted for classical deposition on honeycombs. By this route, suspensions with a high solids content can be prepared and consequently, a high quantity of washcoat can be deposited in a single impregnation step. The synthesis and characterization of doped-ceria powders from both metallo-organic and inorganic precursors, have been described in detail,[36,37] where it was shown that sol-gel derived powders had very attractive physico-chemical characteristics; in particular they exhibited a uniform microstructure, containing very small ceria crystallites ($\leqslant 10$ nm), which can be maintained up to 1000°C. Oxygen mobility and catalytic activity were found to depend on the powder composition and on the type of precursor used for the preparation of sols (metallo-organic or inorganic). The basic molar composition of the most attractive powder was $(CeO)_{0.25}(CaO)_{0.02}(Al_2O_3)_{0.73}$. This powder was prepared from metallo-organic precursors and contained noble metals (1.36 wt.% Pd and 0.14 wt.% Rh) inserted at the sol-stage. After drying, the powder was calcined at 700°C and then ball-milled until its characteristic diameter d_{90} was reduced to 3.9 μm (milling time required: 60 hours). The fine powder was dispersed in water with the aid of Darvan C (R.T. Vanderbilt Co., Norwalk, CT, USA), and slurries with 35 wt% solids content were then used for coating the honeycombs.



(a)

(b)

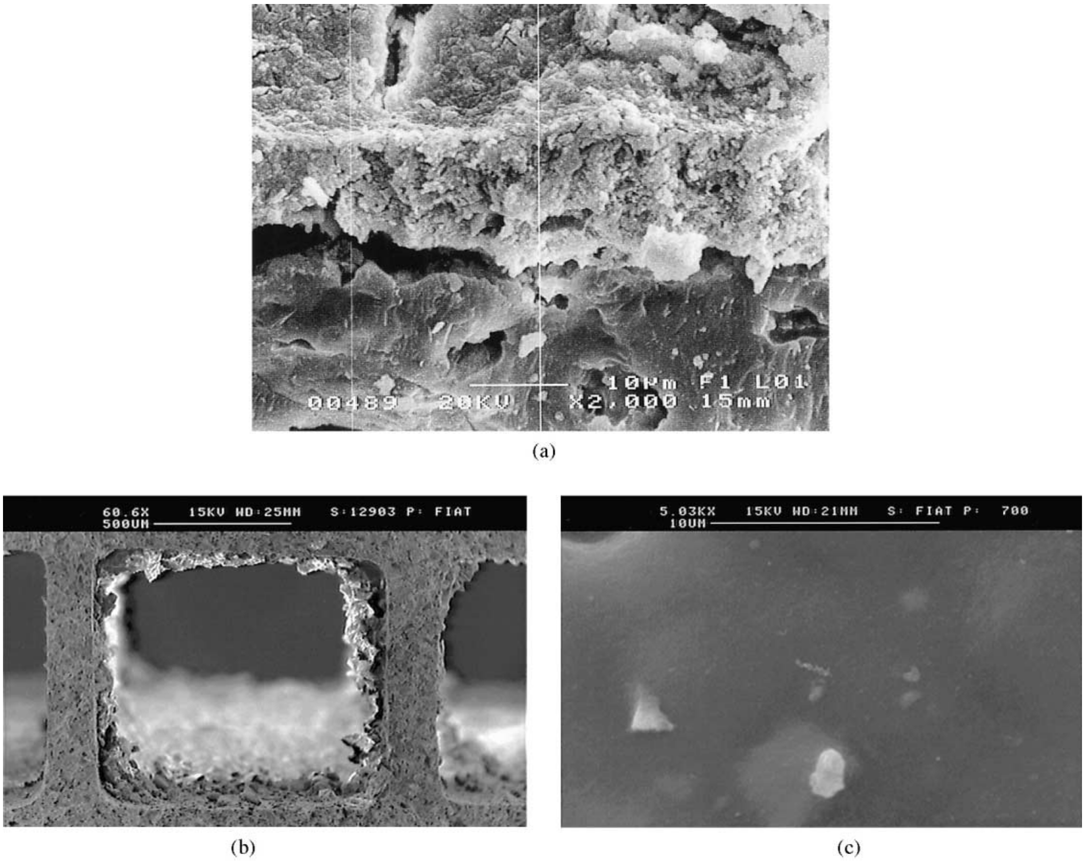
Fig. 6. Typical morphology of honeycomb coated with powder obtained by the polymeric sol-gel route, with composition $(CeO)_{0.25}(CaO)_{0.02}(Al_2O_3)_{0.73}$/1.36 wt.% Pd/0.14 wt.% Rh, calcined at 700°C and grinded to $d_{90} = 3.9$ μm: (a) Morphology of a coated channel wall, (b) substrate-washcoat interface.

A significantly higher loading percentage (13–15 wt.% per impregnation) was achieved in this case. Such a honeycomb coated only once with a slurry of sol-gel-derived doped-ceria powder is shown in Fig. 6a. The uniformity of the thickness of the deposited washcoat layer along both sides of the channel wall can be clearly observed. The magnification of the washcoat/honeycomb interface (Fig. 6b) reveals that the washcoat is about 20 μm thick. The deposited particles consist of small aggregates of nanophase powder, are of few microns in size and form a tightly anchored, interconnected layer. The washcoat microstructure is much less compact, coarser and therefore of lower adhesion quality than that obtained directly from sols (Fig. 5b vs. Fig. 6b).

3.1.3. *Washcoating with hybrid sol-powder systems*

As mentioned above, the main problems associated with loading directly from sols, i.e. sol infiltration in the support and low loading per impregnation, can be avoided with the use of powder slurries. However, at least one more firing step is required for powder preparation, followed by extensive milling for reducing the size of aggregates in order to prepare homogeneous suspensions and firmly adhered washcoat layers. An alternative to the two methods mentioned above is to use sols as suspension media for the sol-gel derived powders, and to impregnate honeycombs with these hybrid systems. This method can combine the high loading per impregnation achieved with slurries, with the fine microstructure and good adhesion of sol-gel derived layers.

Two hybrid systems were used in the present study: the first one was produced by mixing a slurry of commercial γ-alumina powder (powder particle size $d_{90} = 2.1$ μm, slurry solids content 35 wt.%) with the inorganic calcia-ceria based sol. The proportions of sol and powder were such to correspond to the selected $(CeO)_{0.25}(CaO)_{0.02}(Al_2O_3)_{0.73}$ stoichiometry after the firing treatment. Because of the high solvent content and absence of binder, the “as-prepared” sol-slurry mixture had a very low viscosity. The mixture was progressively concentrated by controlled evaporation, and loading experiments were performed with various concentration levels. The honeycomb loading percentage achieved as a function of sol concentration is reported in Fig. 3 compared to results obtained for direct depositions of sols alone. Such a hybrid system obviously improves the loading achieved per impregnation compared to impregnations with sols.



(a)

(b)

(c)

Fig. 7. Hybrid sol-powder systems: (a) substrate-washcoat interface of a monolith coated with γ-alumina powder dispersed in colloidal doped-ceria sol, (b) front view of a honeycomb coated with sol-gel polymeric ceria powder dispersed in colloidal doped-ceria sol, (c) magnification on washcoat surface of (b) above.

The obtained loading percentage varies between 6 and 8 wt.% per impregnation, values intermediate between those obtained for the other two cases (sols and sol-gel powder suspensions). The substrate/washcoat interface of a monolith coated with such a hybrid system is shown in Fig. 7a (same magnification as Figs. 5a and 6b). The washcoat layer is about 10 μm thick and its morphology is intermediate between those shown in Figs 5 and 6: the coarser alumina particles are dispersed within a gel-like ceria matrix which seems to "bind" the particles together. The advantage of using both powders and sols is two-fold: on the one hand the sol phase is actually forming "bridges" between the powder particles improving their adhesion; on the other hand the alumina particles help in preventing the sol from penetrating into the support pores.

The second hybrid system was produced by dispersing 5 wt.% of the ceria based powder described in Section 3.2 (derived from metallo-organic precursors after heat-treatment at 450°C) in the equivalent inorganic sol. The rationale for the choice of this particular composition was to combine the high oxygen mobility and catalytic activity of the powders produced from organic sols [36,37] with the ease of deposition of the inorganic sols. This mixture was employed for coating honeycombs (four impregnations and a final heat-treatment at 700°C for 2 h). Such a loaded honeycomb is shown in Fig. 7b. After the four deposition cycles, a coating 50–150 μm thick can be observed corresponding to a support loading in the range 15–20%. A very high magnification of the washcoat surface (Fig. 7c) reveals also a gel-like layer that seems to embed the powder particles as in the case of the boehmite dispersion. The washcoat layer is also much rougher than the pure sol-gel derived layers, a fact that can improve the contact between the washcoat and the gaseous reactants.

3.2. *Washcoat porous structure*

The loaded honeycombs were characterized with respect to pore sizes distribution with mercury porosimetry and N_2 adsorption–desorption. Representative results are summarized in Fig. 8 where a commercial honeycomb (unknown washcoat loading but in the range 20–50 wt.%) is compared to the series of honeycomb specimens prepared in this work by different loading methods. These honeycombs were loaded with inorganic sol (specimen described in Section 3.1.1., Fig. 5, loading of 7.5 wt.%), with a suspension of sol-gel powder (specimen described in Section 3.1.2., Fig. 6, loading 13 wt.%) and with the hybrid inorganic ceria sol/γ-alumina powder (Section 3.1.3, Fig. 7, loading 6.7 wt.%). As shown in Fig. 8a (Hg porosimetry data), the un-coated support has a mean pore diameter of 10 μm and no significant meso- or microporous volume (Fig. 8b–N_2 desorption data). The mercury porosimetry curves for the coated supports show the combined influence of the support and of the washcoat layer. The presence of the washcoat shifts the apparent mean pore size of the support, towards smaller values. In the case of the honeycomb coated directly from the sol, the step observed at the lower end of the mercury porosimetry curve (0.01 μm) is attributed to the pores from the washcoat. This mercury intrusion curve is very similar to that of the commercial catalyst.

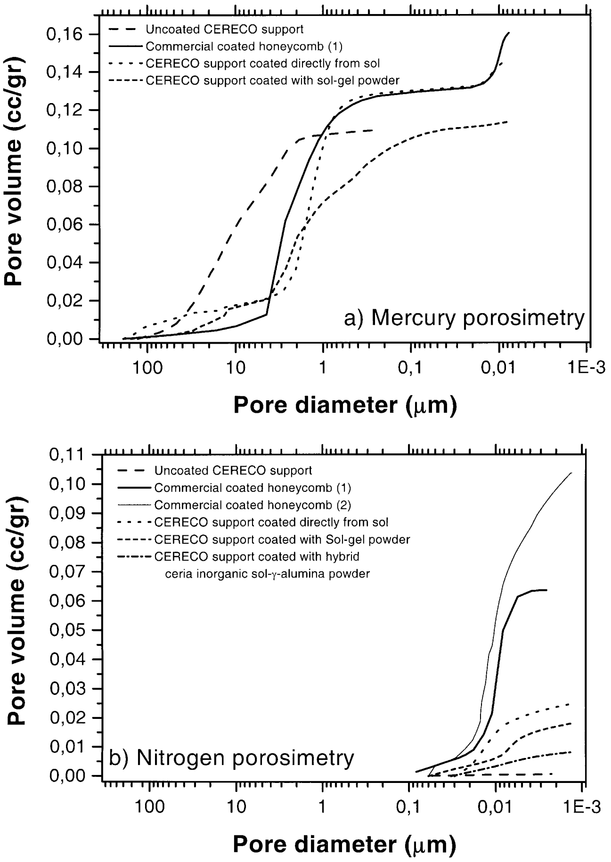
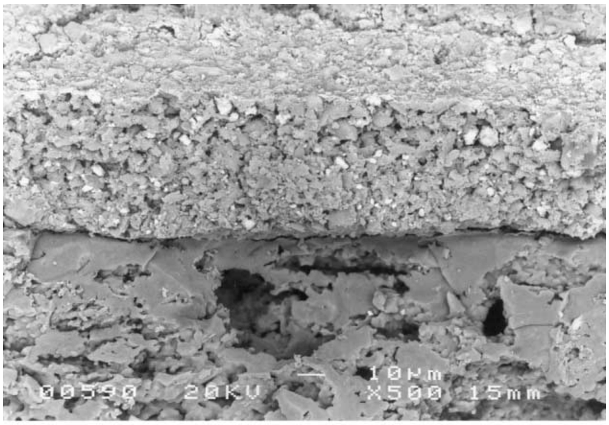
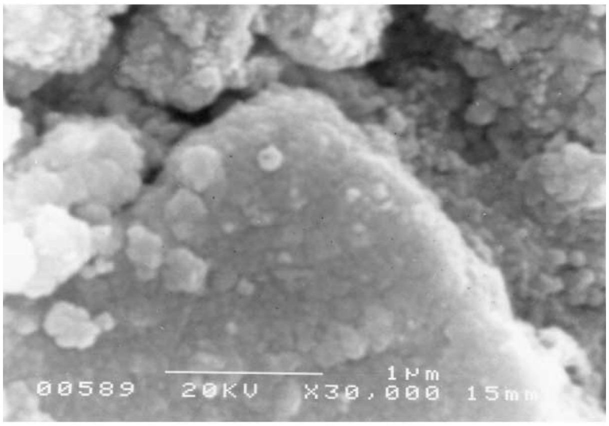


Fig. 8. Comparison of pore size distributions of coated honeycombs in the fresh state: (a) mercury, (b) nitrogen porosimetry.

A clearer picture of the washcoat pore structure is obtained from the nitrogen adsorption curves shown in Fig. 8b. Two curves for commercial catalysts are shown, obtained on two different commercial specimens, in two different laboratories of the authors of the present work. Even though the mean meso-pore diameters obtained are very close to one another, there exists a discrepancy with respect to the total pore volume. This might be due to differences in the measurement conditions such as outgassing temperature and time, etc. Anyway both specimens seem to have similar pore structure. By comparing the pore volume distribution curves (N_2 adsorption) measured for honeycombs coated with sols or with powder suspensions to those obtained for the commercial specimens, it is clear that the latter have the largest pore volume. In agreement to the final part of the Hg porosimetry curves, N_2 adsorption data reveal the presence



(a)



(b)

Fig. 9. Morphology of a commercial catalyst system in consecutive magnifications: (a) support/washcoat interface, 500×, (b) washcoat surface, 30000×.

of meso-pores in the range of 0.015 μm (150 Å), for all the coated specimens. All the coated honeycombs prepared in this work exhibit a similar total pore volume, but the hybrid sol-powder system exhibits a gradual transition from the macro- to the meso-porous region, without any sharp step in the pore size distribution curve, as observed for the other two cases.

The above results clearly fit with the comparative observations of the coating morphology. SEM micrographs of the commercial washcoat (that corresponds to the porosimetry curves marked No 1 in Fig. 8) are shown in Fig. 9. The much higher washcoat loading of the commercial honeycomb is obvious from Fig. 9a, where the washcoat thickness is about 50 μm. Higher magnifications (Fig. 9b) reveal a compact washcoat microstructure of aggregated nano-particles, a fact that suggests the use of a sol phase (comparable to the aqueous sols used in the present study) in combination with powder slurries for loading. This can also account for the high meso-porosity of the commercial washcoat (Fig. 8). Such a high meso-porosity was typically measured for the sol-gel derived coatings tested in the present study. Consequently, sol-gel derived systems can definitively produce coated honeycombs with microstructure and pore volume comparable to those of current commercial catalysts.

All the systems deposited were subsequently tested with respect to catalytic activity and thermal aging. A detailed presentation of the results is the subject of the second part of the work.[20] It should be briefly mentioned here, however, that ceria-based catalytic systems with only a small amount of palladium addition proved to be effective catalysts for both CO and hydrocarbon pollutants achieving 99% conversion of CO and propane at temperatures as low as 230°C.[37] With respect to hydrocarbons conversion in particular, sol-gel nano-ceria-based systems prepared in this study, exhibited light-off temperatures between 495 and 512 K, depending on the preparation route. These values are about 70 K higher than those of commercially available systems based on precious metals but were achieved with half the amount of total washcoat and less than half the amount of noble metals, indicating the excellent potential of nano-phase doped ceria as a three-way catalytic component.

4. Conclusions

Sol-gel technology is a very powerful tool for the synthesis of nanophase environmental catalytic systems, such as those based on ceria, because it allows a precise control and tuning of the catalysts microstructure as well as their potential direct deposition on ceramic supports.

The deposition of such systems on honeycombs can, in principle, take place directly from the sol phase. In such a case, precise tuning of the sol viscosity through binder addition and solvent evaporation proved to be necessary for the deposition of a surface layer upon the support channel walls. The washcoat properties were found to depend on the preparation route. Aqueous sols made from inorganic precursors generated coatings of good quality, whereas washcoats obtained from metallo-organic precursors were cracked but consisted of smaller ceria nano-crystallites with a higher oxygen mobility. In both cases, the low loading achieved per impregnation imposed the need for multiple impregnation steps. However, sol-gel methods are typically adapted to the preparation of thin films: cost-effective production of thick films without generating a lot of cracks is difficult. The method, however, could be proved to be among the most attractive ones for the deposition of thin washcoat layers on honeycomb supports with smaller channels, such as those with 1000 cells/in^2 currently targeted in honeycomb industry.

Sol-gel methods were then alternatively used in this work for the synthesis of highly active, dispersible nanophase ceria-based powders and the preparation of high-solid-content aqueous slurries. These slurries were used for honeycomb impregnation, and high loadings were achieved in a single impregnation, at the expense of additional slurry preparation and particle size reduction steps.

Hybrid systems where a sol-gel derived nanophase powder is dispersed in a sol, occurred the most suitable solution in terms of combination of powder nano-phase properties and ease of deposition. Indeed, this combination limits the sol infiltration into the support pores and allows satisfactory loading per impregnation. However, the most significant advantage of these systems is the possible combination of the properties of sols and powders derived from different routes, in order to prepare washcoats with optimal performance. Further advantages of such systems with respect to specific properties such as fine-tuning of the washcoat pore structure and catalytic activity will become evident in the second part of the work.[20]

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References

1. Heck, R. M. and Farrauto, R. J., *Catalytic Air Pollution Control-Commercial Technology*. Van Nostrand Reinhold, New York USA, 1995.
2. Trovarelli, A., Catalytic properties of ceria and CeO_2-containing materials. *Catal. Rev. Sci. Eng.*, 1996, **38**, 439–520.
3. Trovarelli, A., deLeitenburg, C. and Dolcetti, G., Design better cerium-based oxidation catalysts. *Chemtech*, 1997, **27**(6), 32–37.
4. Trovarelli, A., deLeitenburg, C., Boaro, M. and Dolcetti, G., The utilization of ceria in industrial catalysis. *Catal. Today*, 1999, **50**, 353–367.
5. Diwell, A. F., Rajaram, R. R., Shaw, H. A. and Truex, T. J., The role of ceria in three-way catalysts. In *Catalysis and Automotive Pollution Control II, Vol. 71, Studies in Surface Science and Catalysis*, ed. A. Crucq. Elsevier Science, Amsterdam, 1991, pp. 139–152.
6. Oh, S. H., Effects of cerium addition on the CO-NO reaction kinetics over alumina-supported Rhodium catalysts. *J. Catal.*, 1990, **124**, 477–487.
7. DiMonte, R., Fornasiero, P., Kaspar, J., Rumori, P., Gubitosa, G. and Graziani, M., $Pd/Ce_{0.6}Zr_{0.4}O_2/Al_2O_3$ as advanced materials for three-way catalysts. Part I. Catalyst characterization thermal stability catalytic activity in the reduction of NO by CO. *Appl. Catal. B. Env.*, 2000, **24**, 157–167.
8. Farrauto, R. J., Voss, K. E. and Heck, R. M. Ceria–alumina oxidation catalyst. US Patent 5,627,124, 6 May 1997.
9. deLeitenburg, C., Trovarelli, A., Llorca, J., Cavani, F. and Bini, G., The effect of doping CeO_2 with zirconium in the oxidation of isobutene. *Appl. Catal. A. Gen.*, 1966, **139**, 161–173.
10. Terribile, D., Trovarelli, A., Llorca, J., deLeitenburg, C. and Dolcetti, G., The preparation of high surface area CeO_2–ZrO_2 mixed oxides by a surfactant-assisted approach. *Catal. Today*, 1998, **43**, 79–88.
11. Fornasiero, P., Balducci, G., Kaspar, J., Meriani, S., DiMonte, R. and Graziani, M., Metal-loaded CeO_2–ZrO_2 solid solutions as innovative catalysts for automotive catalytic converters. *Catal. Today*, 1996, **29**, 47–52.
12. Vlaic, G., DiMonte, R., Fornasiero, P., Fonda, E., Kaspar, J., Graziani, M.The CeO_2–ZrO_2 system: Redox properties and structural relationships. In *Catalysis and Automotive Pollution Control IV, Vol.116, Studies in Surface Science and Catalysis*, ed. N. Kruse, A. Frennet and J. M. Bastin. Elsevier Science, Amsterdam, 1998, pp. 185–195.
13. Zhang, Y., Andersson, S. and Muhammed, M., Nanophase catalytic oxides: I. Synthesis of doped cerium oxides as oxygen storage promoters. *Appl. Catal. B*, 1995, **6**(4), 325–337.
14. Masui, T., Ozaki, T., Machida, K. and Adachi, G., Preparation of ceria–zirconia sub-catalysts for automotive exhaust cleaning. *J. Alloys. Comp.*, 2000, **303–304**, 49–55.
15. Masui, T., Fujiwara, K., Peng, Y., Sakata, T., Machida, K., Mori, H. and Adachi, G., Characterization and catalytic properties of CeO_2–ZrO_2 ultrafine particles prepared by microemulsion method. *J. Alloys Comp.*, 1998, **269**, 116–122.
16. Masuda, K., Kawai, M., Kuno, K., Kachi, N. and Mizukami, F., Preparation and catalytic effects of CeOx–Moy–Al_2O_3 (M = Ba, La, Zr and Pr) by an improved sol-gel method for automotive catalysts. In *Preparation of Catalysts V*, ed. G. Poncelet, P. A. Grange, P. Grange and B. Delmon. Elsevier Science, Amsterdam, 1991, pp. 229–238.
17. Murrell, L. L. and Tauster, S. J., Sols as precursors to transitional aluminas and these aluminas as host supports for CeO_2 and ZrO_2 micro-domains. In *Catalysis and Automotive Pollution Control II, Vol. 71, Studies in Surface Science and Catalysis*, ed. A. Crucq. Elsevier Science, Amsterdam, 1991, pp. 547–555.
18. Rossignol, S., Madier, Y. and Duprez, D., Preparation of zirconia-ceria materials by soft chemistry. *Catal. Today*, 1999, **50**, 261–270.
19. Guizard, C. G., Julbe, A. C. and Ayral, A., Design of nanosized structures in sol-gel derived porous solids. Applications in catalyst and inorganic membrane preparation. *J. Mater. Chem.*, 1999, **9**, 55–65.
20. Agrafiotis, C., Tsetsekou, A., Stournaras, C. J., Julbe, A., Dalmazio, L., Guizard, C., Parussa, F., and DeBenedetti, M., Evaluation of Sol-gel methods for the synthesis of doped-Ceria environmental catalysis systems. Part II: catalytic activity and resistance to thermal aging, submitted to *Appl. Catal. B. Env.*
21. Watkins, W. L. H., Kudla, R. J. and Chatta, M. S., NO_x trap catalyst for lean-burn engines, US Patent 6,129,898, 10 October 2000.
22. Abe, F., Noda, N., Hori, M. and Fukui, T., Catalyst for exhaust gas purification and process for production thereof. US Patent 5,439,865, 8 August, 1995.
23. Suzuki, T. and Sobukawa H., Composite oxide, composite oxide carrier and catalyst. US Patent 6,150,288, 21 November, 2000.
24. Marella, M., Meregalli, L. and Tomaselli, M., Sol-gel process for obtaining pure and mixed oxide zirconia spheres, microspheres and washcoats, useful as catalysts or catalyst supports, US Patent 5,750,459, 12 May, 1998.
25. Narula, C. K., Watkins, W. L. H. and Shelef, M., Aluminum oxide catalyst supports from alumina sols. US Patent 5,210,062, 11 May, 1993.
26. Mulder, A., van Looy, F. and Geus, J.W., Catalyst or membrane precursor systems, catalyst or membrane systems and method of preparing such systems. US Patent 5,472,927, 5 December, 1995.
27. Najjar, M. S. and Hilmar M. D., Method of forming membranes useful for separation of gases. US Patent 5,160,352, 3 November, 1992.
28. Guizard, C., Julbe, A., Larbot, A. and Cot, L., Ceramic membrane processing. In *Chemical Processing of Ceramics*, ed. E. J. A. Pope and B. I. Lee. Marcel Dekker, New York, 1994, pp. 501–531.

29. Guizard, C., Julbe, A., Ayral, A., Ramsay, J. and Larbot, A., Recent advances in Ceramic Membrane Processing, In *Ceramics: Charting the Future,* ed. P. Vincenzini, Techna Srl, 1995, pp 2743–2754.
30. Guizard, C., Mouchet, C., Vacassy, R., Julbe, A. and Larbot, A., Sol-gel processing of inorganic membranes. *J. Sol-Gel Sci. and Technol*., 1994, **2**, 483–487.
31. Cini, P., Blaha, S. R., Harold, M. P. and Venkataraman, V., Preparation and characterization of modified tubular ceramic membranes for use as catalyst supports. *J. Membr. Sci*., 1991, **55**, 199–225.
32. Murrell, L. L., Sols and mixtures of sols as precursors of unique oxides. *Catal. Today*, 1997, **35**, 225–245.
33. Suzuki, H., Yokota, K., Iijima, T., Suzuki, T., Kasahara, K. and Tatyeishi, S, Catalyst for purifying exhaust gases and process for purifying exhaust gases. US Patent 5,575,983, 19 November, 1996.
34. Suzuki, H., Matsumoto, S., Miyoshi, N., Ishibasi, K., Kasahara, K., Tateishi, and Suzuki, D., Catalyst for purifying exhaust gases. US Patent 6,159,897, 12 December, 2000.
35. Yoshida, T, Murachi, M., Tsuji, S. and Taguchi, N., High heat-resistant catalyst with a porous ceria support. US Patent 5,972,830, 26 October, 1999.
36. Julbe, A., Dalmazio, L., Guizard, C., Berjoan, R., Kiely, C., Burrows, A. and Pirjamali, M., Evaluation of Sol-gel methods for the synthesis of CeO_2-based materials with enhanced oxygen mobility, submitted to *J. Mater. Chem.*
37. Dalmazio, L., *Synthèse par voie sol-gel et propriétés catalytiques de matériaux nanophasés à base de cérine présentant une mobilité accrue de l'oxygène*, Ph. D. thesis- Montpellier University (UM II), 17/07/00.
38. Agrafiotis, C., Tsetsekou, A., Stournaras, C. J., Julbe, A., Dalmazio, L. and Guizard, C., Deposition of nanophase doped-Ceria systems on ceramic honeycombs for automotive catalytic applications. *Sol. State Ionics*, 2000, **136–137**, 1301–1306.
39. Ekonomacou, A., Tsetsekou, A. and Stournaras, C. J., An investigation of the processing parameters for cordierite honeycombs production. In *Ceramics: Charting the Future,* ed. P. Vincenzini. Techna S.r.l., 1995, pp. 2439–2448.