The effect of powder characteristics on washcoat quality. Part I: Alumina washcoats

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Abstract

The adhesion of γ-alumina washcoats on cordierite honeycombs was investigated with the aim to correlate the adhesion properties to the characteristics of the deposited powders, and, determine the conditions that can ensure integrity and endurance of the substrate/washcoat system under the severe operating conditions of an automobile catalytic system. It is shown that adhesion depends primarily on the particle size of the deposited powder. Depending on the production method, some powders have the form of large agglomerates and, if deposited as such upon the honeycombs, exhibit very poor adhesion properties. Reduction of the agglomerates' size down to the order of a few (2–5) microns is necessary in order to ensure adhesion comparable to that of commercial catalysts. Particles of colloidal dimensions exhibit excellent adhesion to the support, provided that reduction of the agglomerates' size that they form during calcination, takes place before deposition. © 2000 Elsevier Science Ltd. All rights reserved.

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1. Introduction

In the automobile catalytic converter assembly, the honeycomb ceramic support is coated with a material of high surface area called the washcoat, which acts as a host for the noble metal catalysts. Besides the high surface area, other desirable washcoat properties are thermal stability and appropriate pore size distribution. A material combining these properties and thus, most widely used in this kind of application is γ-alumina.[1] The washcoat phase usually contains smaller quantities of other phases, which have a particular function. For example, ceria,[2,3] and lanthania[4] are frequently added to γ-alumina in order to induce oxygen storage capacity and thermal stability respectively.

The washcoat is usually applied on the honeycomb by impregnation of the honeycomb in a suspension (slurry) of the powder and subsequent drying and calcination.[5] In the case of γ-alumina, instead of slurries of the calcined γ-alumina powder, slurries of dispersible pre-cursor powders such as aluminum hydroxide (Al(OH)$_3$) or boehmite (γ-AlOOH)[6] are often used. These powders, upon calcination, expel water and are transformed to γ-alumina. Removal of the excess slurry from the substrate channels, drying and subsequent calcination around 600°C are employed for the formation of a solid γ-alumina washcoat layer on the honeycomb walls. Having optimized the slurry properties such as solids content, pH and viscosity, the loading of honeycombs with the required amount of washcoat is usually achieved with few impregnations.[7]

Another method for the coating of substrates is the sol-gel method where, instead of powders, liquid precursor materials (sols) are used. Not only extremely active materials can be effectively synthesized in this way, but incorporation of other phases such as promoters or stabilizers can be greatly facilitated and controlled. The impregnation of the honeycombs can be done directly with a sol; upon drying and calcination of the monolith, a well-adhered washcoat layer can be formed in situ upon the support walls. This method is widely used for the preparation of membranes on ceramic substrates of various geometries such as discs,[8] cylinders,[9] hollow tubes[10,11] and honeycombs.[12] By this route the synthesis of dispersible powders and the

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preparation of slurries are avoided ; however, problems of other kinds can appear. These are the low monolith loading per impregnation,[10,11] the cracking and subsequent "peeling" of the washcoat layer due to the loss of large amounts of volatile compounds during calcination, and the penetration of the sol in the porous structure of the support making the catalyst less accessible to the gaseous reactants. Saracco and Montanaro[10,11] have impregnated porous alumina tubes with alumina sols for the preparation of catalytic filters. They observed significant penetration of the sol into the porous structure of the support and complete pore blockage. This problem can be resolved with precise adjustment of the sol viscosity with the addition of various binders.[8,13]

In order to combine the advantages of sol-gel synthesis with the ease of loading with slurries, sol-gel made powders can be prepared by drying and calcination of the respective gels, and subsequently can be processed as suspensions (slurries) for their deposition upon honeycombs. These powders can have a higher surface area and enhanced activity compared with "conventionally" synthesized ones.[12] Even though there are many studies dealing with the synthesis of thermally stable alumina powders via sol-gel methods, the catalytic activity and thermal stability tests of these systems are performed with alumina in the form of powder or pellets;[14–16] studies are not concerned with the deposition of such systems upon honeycomb structures. The preparation of stable slurries of the washcoat powders, and the optimization of their rheological properties are essential for an effective deposition of a homogeneous and uniform washcoat layer.

The severe conditions of actual operation (hot exhaust gases of high velocity, mechanical vibrations) can lead to detachment of the washcoat layer (and of the noble metals that it contains) and consequent degradation of the catalyst efficiency. Thus, in addition to the microstructural requirements for a washcoat material, excellent adhesion to the substrate is a further crucial requirement and optimization of the parameters that affect the adhesion of the washcoat layer on the support is imperative. However, very few studies have addressed the problem of adhesion quality between the washcoat film and the porous support. Cini et al[9] have deposited γ-alumina membranes on hollow α-alumina tubes in order to prepare supports for catalytic applications. They used a boehmite sol as the coating medium and studied the effect of alumina content and sol viscosity on the thickness and the quality of the film produced. They concluded that an optimal combination of low viscosity and high alumina concentration could be used to produce crack-free films provided though, that the film thickness was kept below 10 μm.

In a previous work[17] we have reported preliminary results on adhesion studies of various washcoats on cordierite honeycombs. In this study, the adhesion of γ-alumina washcoats deposited from aqueous dispersions of powders (slurries) is investigated with the aim of correlating the coating quality with the powder characteristics. The washcoats were prepared both from commercially available powders, as well as from powders synthesized by sol-gel methods, so that comparisons on the effect of the powder microstructure on adhesion characteristics could be made.

2. Experimental procedure

For the preparation of alumina washcoats several raw materials were employed. A commercial γ-alumina powder (Pechiney, Greece) which is a by-product of the Bayer process was employed in most of the experiments. In order to compare the effect of the powder origin and properties on the washcoat characteristics, two kinds of precursor powders were used, namely aluminum hydroxide ($Al(OH)_3$ — Merck GmbH, Darmstad, Germany) and boehmite (γ-AlOOH — Disperal, Condea, Germany). These two kinds of powders are essentially the more- and less-hydrated forms of aluminum oxide ($Al_2O_3*3\ H_2O$ and $Al_2O_3*H_2O$ respectively) and upon calcination at temperatures in the range 500–700°C, they are converted to the γ-alumina phase. In addition, a sol-gel made γ-alumina powder, prepared via hydrolysis, gelation and peptization of an aqueous sol of aluminum nitrate and calcined in the same temperature range was examined.

Aqueous slurries of the powders were prepared with solids content 35 wt%, based on the results of studies on the optimization of the slurry properties for a uniform deposition, which are described in a previous work.[7] For slurry stabilization either HCl or the ammonium salt of the poly-methacrylic acid (NH_4-PMA- commercial name Darvan C, R. T. Vanderbilt Co., Norwalk, CT, USA) were used as dispersants. In order to identify the effect of particle size on adhesion, the powder slurries were ball-milled for various periods of time until batches with the desired particle size distribution were obtained. In order to avoid impurities pickup during milling, ball-milling was carried out in water, with α-alumina grinding media, in containers from hard plastic material. Particle size distributions of the powders were measured with the aid of a laser particle size analyzer (Malvern E- 3600) as well as with the aid of scanning electron microscopy (JEOL – 6300 microscope). Scanning electron microscopy (SEM) was also used for the study of the morphology of the starting powders as well as of the coated honeycombs.

Subsequently, cylindrical cordierite samples manufactured by CERECO, with 400 square cells/in^2 were impregnated in the slurries, under stirring, for 1 min. In most of the experiments five specimens of 1.5 cm diameter and 2 cm length were employed. All the cordierite
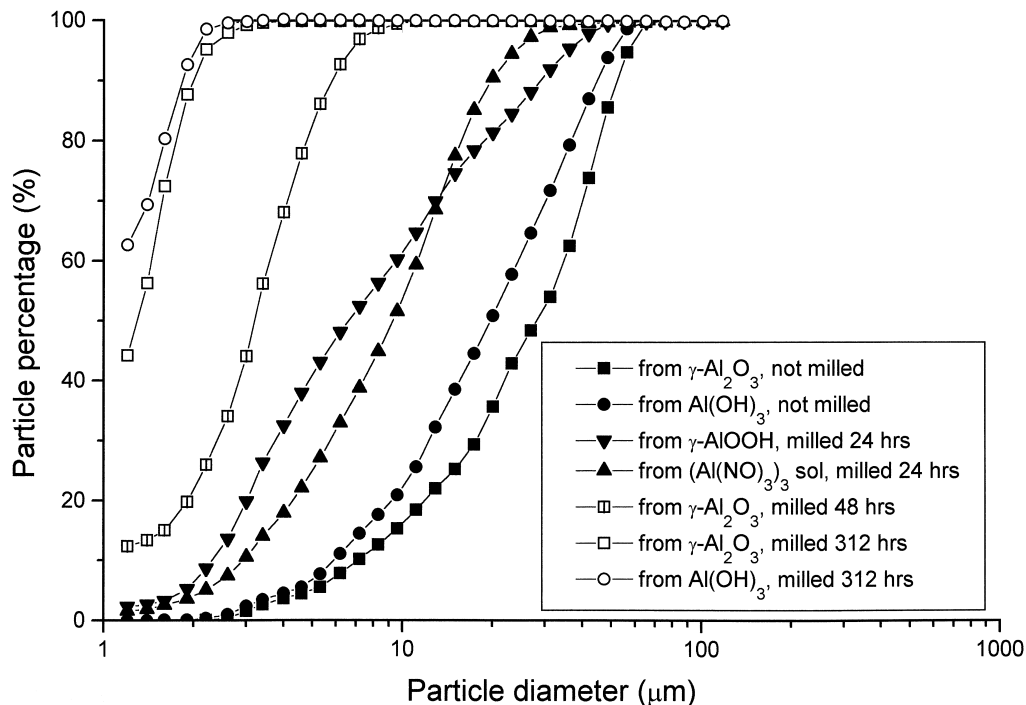
Fig. 1. Effect of milling time on particle size distribution for the commercial γ-alumina powder and for γ-alumina powders produced from the various precursor materials after calcination at 600°C for 2 h.

specimens had a porosity of 13% and a mean pore size diameter of 10 μm as determined with the aid of mercury porosimetry (Quantachrome, AUTOSCAN 200 porosimeter). The loaded specimens were withdrawn and excess slurry was removed by blowing air through the honeycomb channels. Then the specimens were dried at 110°C for 1.5 h and finally calcined at 600°C for 2 h. Loading percentage was determined from the increase of specimen weight after calcination.

Adhesion of the washcoat layers upon the monolith walls was studied by exposing the loaded monoliths in a stream of hot air in a small laboratory reactor simulating the car exhaust system (reactor temperature = 800°C, free volume velocity = 100,000 h^{-1}) and measuring their weight loss as a function of time. SEM was also employed for an assessment of the quality of the washcoat layer before and after the adhesion tests. The phase composition of the powders was studied by X-ray diffraction using Cu K_a radiation (Siemens D-500 diffractometer). The respective specific surface areas were measured with the aid of Nitrogen porosimetry (Micromeritics ASAP 2000 Instrument)
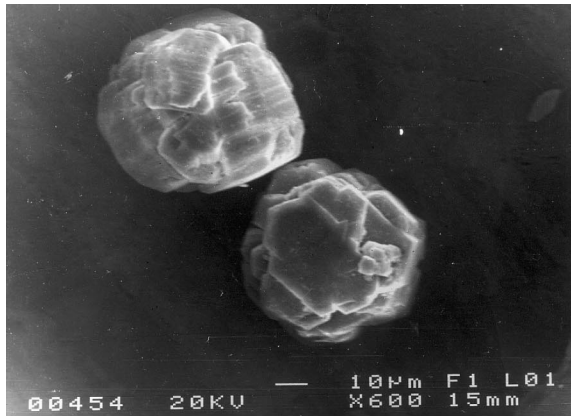
3. Results and discussion

3.1. Powder characterization

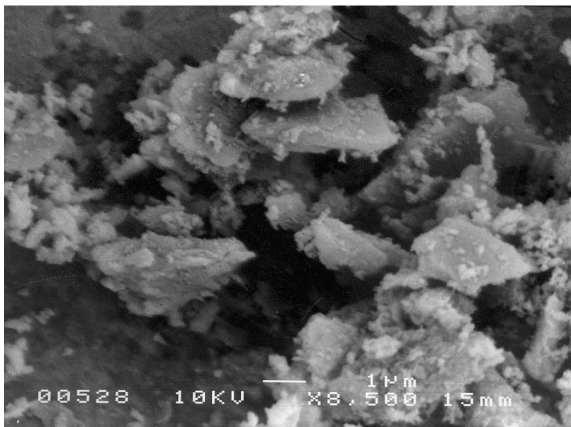Thermal analysis of all three precursor powders, (aluminum hydroxide, boehmite and the powder

obtained from the aluminum nitrate sol) showed that all the weight losses and the relevant phase transformations to γ-alumina are completed at temperatures below 600°C. Thus, all the precursor powders were calcined at 600°C for 2 h in order to be converted to the γ-alumina phase. Calcination has as a result, crystallite growth and formation of coarser particles. The powders obtained from the precursor materials were compared to the commercial one with respect to particle size distribution and morphology. Wet milling of all the powders was employed in order to reduce the particle size and obtain batches of powder with various characteristic diameters.

The curves describing the particle size distributions of the various powders as a function of milling time are shown in Fig. 1. Particle size analysis of the as-received γ-alumina powder indicated a characteristic diameter d_{90} (90% of the powders of the batch are smaller than that) of 52 μm. Even though with only 48 h of milling the characteristic diameter was reduced below 6 μm, extensive milling time (312 h) was required for further reduction down to the order of 2 μm. The same extensive milling time (312 h) was required for size reduction of the powder produced from $Al(OH)_3$ from its initial characteristic diameter down to 1.8 μm.

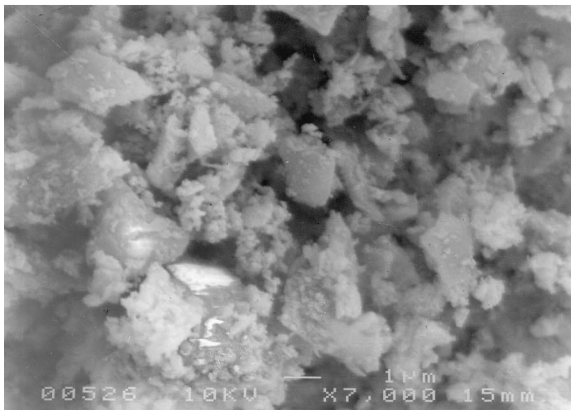SEM photographs of the initial as-received γ-Al_2O_3 powder and of the two finer batches obtained ($d_{90} = 6$ μm and $d_{90} = 2$ μm) are depicted in Figs. 2(a)–(c) respectively. The as-received powder is in the form of large agglomerates, which consist of smaller platelet-like

Fig. 2. SEM photographs of the commercial γ-alumina powder : (a) as-received, (b) after milling for 48 h, (c) after milling for 312 h.

units. As it can be seen in the case of the finer batches, ball-milling breaks down these agglomerates, and finer particle size distributions are obtained, where agglomerates of irregular shape and of a size of few (1–10) coexist with many smaller particles with diameters around 1 μm.

The powders produced from the three precursor materials, (Al(OH)$_3$, γ-AlOOH, sol of aluminum nitrate) after calcination at 600°C for 2 h, are compared in Fig. 3(a), (b) and (c) with respect to their size and morphology (magnification of 10,000 times), whereas in Fig. 3(d), (e) and (f) (magnification of 40,000 times) details of their microstructure are shown. The powder from Al(OH)$_3$ shown in Fig. 3(a), has been ball-milled for 312 h. This has resulted in the formation of a fine, uniform particle size distribution with particles less than 2 μm. On the contrary, the powders from γ-AlOOH (Fig. 3(b)), and from the aluminum nitrate sol (Fig. 3(c)) have been milled only for 24 h and thus they still have the form of larger agglomerates with dimensions in the range 1–5 μm. These observations are in accordance with the respective particle size distribution curves (Fig. 1).

As it can be seen in Figs. 3(d)–(f), all three powders produced from precursor materials share a common characteristic : they consist of very fine individual grains, less than 100 nm. The difference among them is the extent of agglomeration of these grains to the formation of larger particles (which subsequently will be deposited upon the honeycomb substrate). For the case of the powder produced from Al(OH)$_3$, (Fig. 3(d)) extensive milling had as a result the reduction of the size of the agglomerated particles down to very small dimensions: few particles exceed 500 nm. On the contrary, even though the powder from γ-AlOOH, consists also of very fine grains with uniform size around 100 nm (Fig. 3(e)), these still remain connected in larger porous agglomerates. In the case of the powder obtained from the aluminum nitrate sol (Fig. 3(c) and (f)) the grains are agglomerated together in larger, denser entities that also reach a few microns. Individual grains are less than 100 nm, but they coalesce to form somewhat larger, quasi-hexagonal units with dimensions around 500 nm, which in turn are bound together in a dense larger agglomerate. In summary, the basic difference among the three kinds of powders is that even though they all consist of nanometer-size units, in the case of the
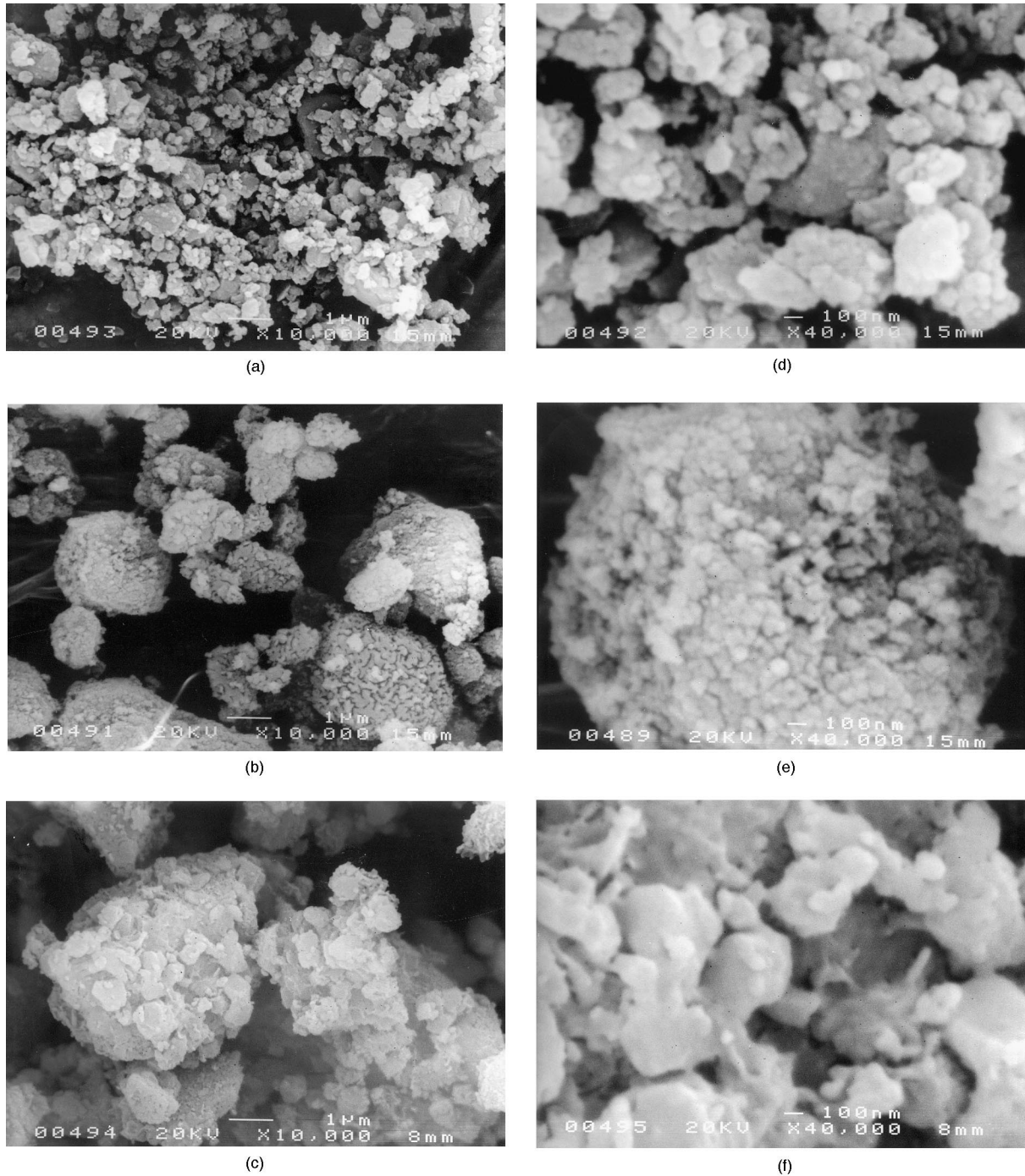
Table 1
Specific surface areas (m^2/g) of the various γ-alumina washcoat powders before deposition and after calcination at 800°C

Powder type	Specific surface area (m^2/gr)	
	Calcination :600°C — 2 h	Calcination :800°C — 16 h
Commercial γ-Al$_2$O$_3$	81.8	65
From Al(OH)$_3$	186.0	125
From γ-AlOOH	173.2	120
From Al(NO$_3$)$_3$ sol	267.0	131

Fig. 3. Size and morphology of γ-alumina powders obtained from various precursor materials after calcination at 600°C for 2 h : (a) Powder from Al(OH)₃, milled for 312 h, (b) powder from γ-AlOOH, milled for 24 h, (c) powder from aluminum nitrate sol, milled for 24 h, (all under magnification of 10,000 times), (d), (e), (f) the respective powders as in (a), (b), (c) above, under magnification of 40,000 times.

Al(OH)₃₋ produced powder, the agglomerates' size has been reduced down to the range of few hundred nanometers prior to deposition.

This difference between the commercial powder and the ones obtained from precursor materials is reflected on the relevant specific surface areas shown in Table 1. The powders from precursor materials are characterized from high values of surface area, with the powder from

the sol exhibiting the highest one, indicating a potential advantage of sol-gel synthesis. Samples of all the powders were subsequently calcined at 800°C for 16 h in order to evaluate their surface loss as well as any changes in their phase composition under the conditions of the adhesion test. As it can be seen from the surface area values reported in Table 1, all the precursor-made powders exhibit a significant loss of surface area after prolonged
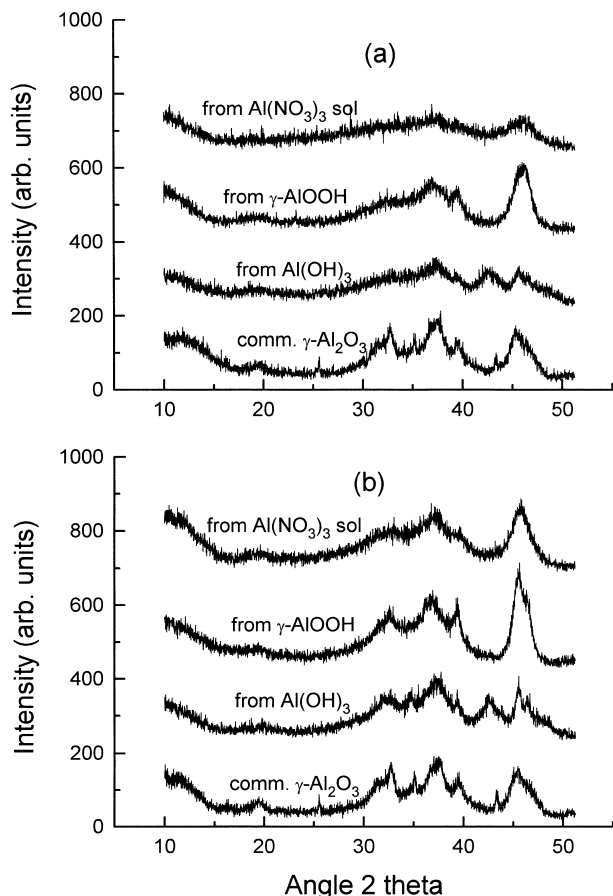
Fig. 4. Phase composition of the various powders: (a) before deposition on the honeycombs (calcination at 600°C for 2 h), (b) after calcination at 800°C for 16 h.

Fig. 5. Weight loss curves of washcoats from the commercial γ-alumina powder, as a function of particle size.

exposure at higher temperatures. The respective surface areas at 800°C are still higher than that of the commercial powder, but probably they would suffer from further loss at higher temperatures. This indicates the need for thermal stabilization of these powders with the addition of the proper stabilizing compounds.

The phase composition of the powders deposited upon the honeycombs can be compared in Fig. 4(a). As expected, the powders from precursor materials exhibit much lesser degree of crystallization than the commercial one, with the powder from the aluminum nitrate sol being the most "quasi-amorphous". At the higher calcination temperature, (800°C — Fig. 4(b)), the peaks of γ-alumina are observed and the powders from precursor materials look much more similar to one another as well as to the commercial one. The large surface area differences observed at 600°C tend to be eliminated at this higher calcination temperature.

3.2. Adhesion studies

Representative weight loss curves of pellets loaded with the commercial γ-alumina washcoats of different particle sizes are shown in Fig. 5 and are compared to the
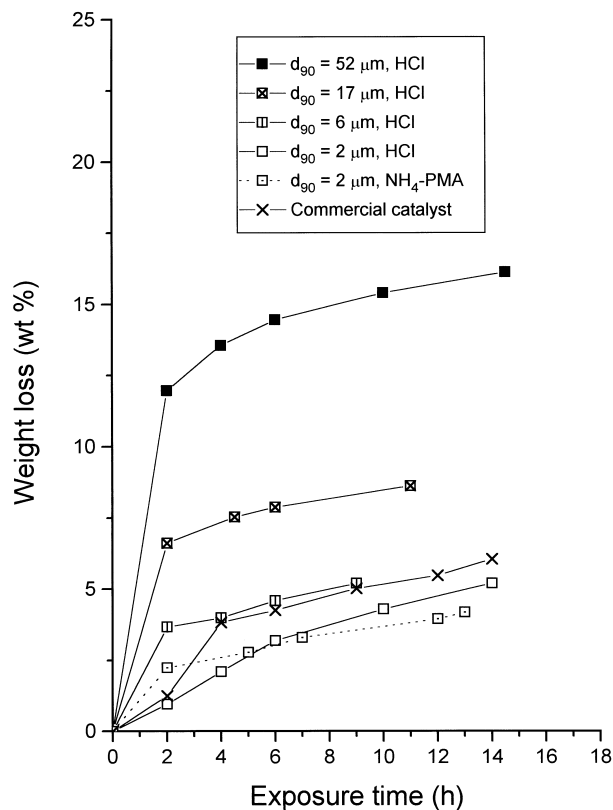
respective curve of a commercial catalyst. Adhesion characteristics seem to depend strongly on the particle size. The washcoats obtained with slurries of the as-received powder ($d_{90} = 52$ μm) exhibit significant weight losses : around 16 wt% after 16 h exposition in the stream of hot air. As the particle size (d_{90}) is reduced to 17 μm, weight losses are limited to 8%. Further reduction of the particle size down to 6 μm results in a weight loss of only 4% — comparable to that of the commercial catalyst. Finally, weight losses less than that of the commercial catalysts were achieved when the particle size (d_{90}) was reduced to 2 μm. On the contrary, the effect of the dispersant used does not seem to be significant. Slurries of the finest particles with the addition of either HCl or NH_4-PMA, exhibited similar weight losses.

The difference in adhesion characteristics between the washcoat and the substrate for the two cases of $d_{90} = 6$ μm and $d_{90} = 2$ μm can be clearly seen in the relevant SEM photographs of the substrate-washcoat interface (Fig. 6(a)–(d)) compared at magnifications of 3000 and 15,000 times. In both cases, the alumina particles are adhered to the outside surface of the channel following the wall curvature (Fig. 6(a) and (b)). Essentially a filtration process takes place where the first layer of the particles is adhered on the outer surface of the channel with only a small fraction of the washcoat powder penetrating into the open pores close to the surface. The
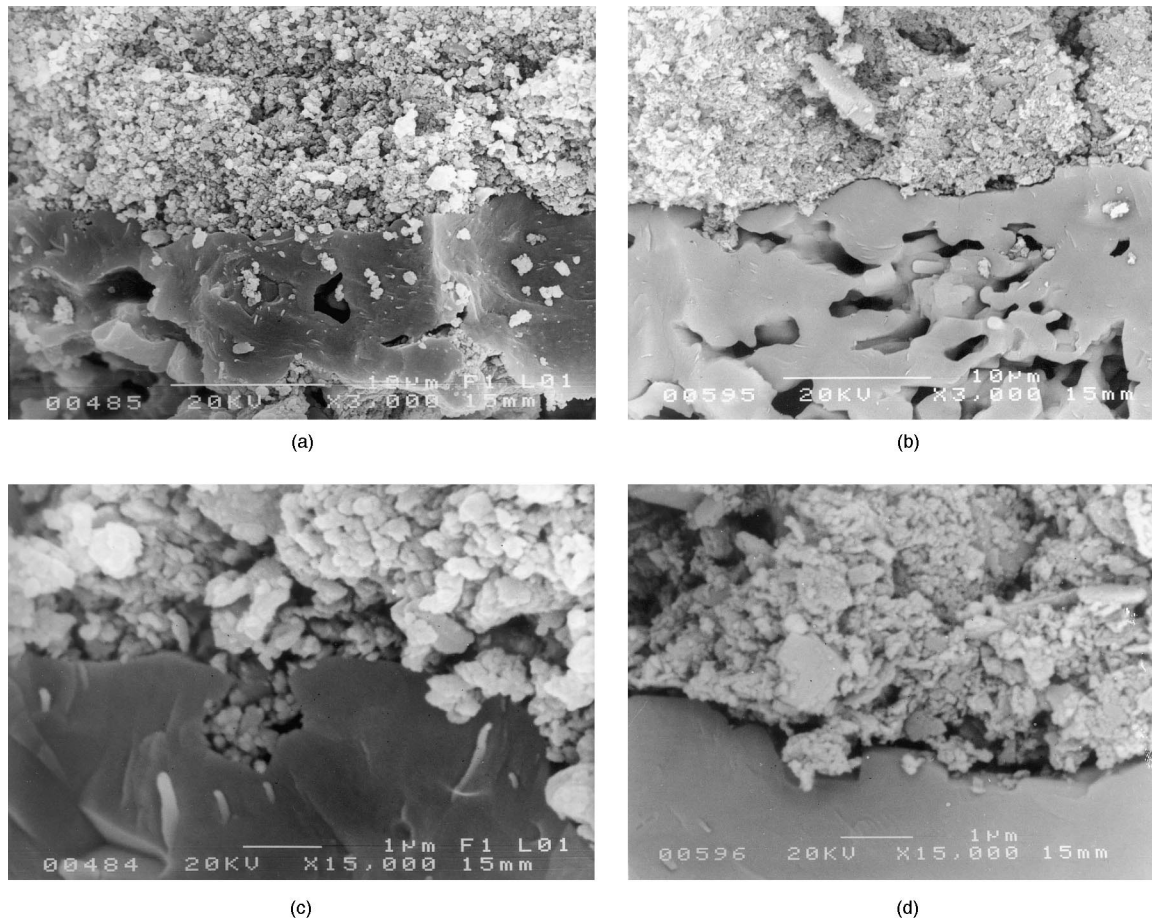
Fig. 6. SEM photographs of the substrate/washcoat interface for the two cases of commercial γ-alumina powders: (a) $d_{90} = 6$ μm, magnification 3000 times (b) $d_{90} = 2$ μm, magnification 3000 times (c) $d_{90} = 6$ μm, magnification 15,000 times (d) $d_{90} = 2$ μm, magnification 15,000 times.

penetration depth is limited in a small region close to the surface. This partial penetration provides for better anchoring of the washcoat on the substrate surface. Successive alumina particles are prevented from entering the pores and get deposited on top of each other forming a "cake" on the outside surface of the channel. At the larger magnifications (15,000 times) shown in Figs 6(c) ($d_{90} = 6$ μm) and (d) ($d_{90} = 2$ μm) the surface irregularities of the substrate walls (small cavities, open pores etc.) with dimensions of the order of 1 μm can be observed. Washcoat particles of adequately small size have penetrated into these surface cavities with which they get interlocked and mechanically "anchored" being very difficult to get removed.

As the "cake" layer is progressively built up, adhesion of the washcoat depends on how well the layers of deposited particles are interlocked with each other. In the case of $d_{90} = 6$ μm (Fig. 6(a)), the higher percentage of larger agglomerates has resulted in a looser particle packing compared to the case of $d_{90} = 2$ μm (Fig. 6(b)). The tighter the packing, the stronger are the forces that develop between neighboring particles, forces that can be either of mechanical, or of interfacial nature. Thus, a tighter packed washcoat layer (such as the one obtained

from the powder of $d_{90} = 2$ μm) of fine particles should exhibit better adhesion.

The difference in morphology between the washcoats obtained with coarser and finer particles can be also observed at the SEM photographs of the top surface of the covered substrate channels in Fig. 7(a) and (b) respectively. For comparison, the morphology of a commercial catalyst is shown in Fig. 7(c), under the same magnification of 3000 times. In the case of the coarser particles there exists a significant amount of agglomerates (of size between 5 and 10 μm) that are spread on the top surface and are loosely bound to the rest of the layer. Thus, they can be carried away from the stream of hot air much more easily. On the contrary, the extensive milling has eliminated these larger agglomerates from the batch of $d_{90} = 2$ μm and has resulted in a fine, uniform and, relatively smooth microstructure, which exhibits excellent adhesion to the substrate. The commercial washcoat exhibits a much coarser particle size distribution than the washcoat with $d_{90} = 2$ μm, a fact to which the higher weight losses could be attributed.

The weight loss curves of the washcoats prepared from the different precursor powders are shown in Fig.
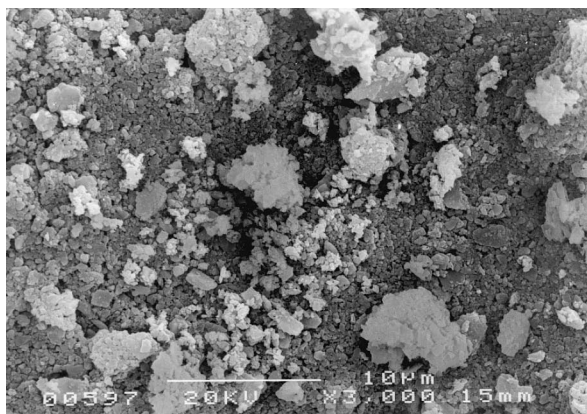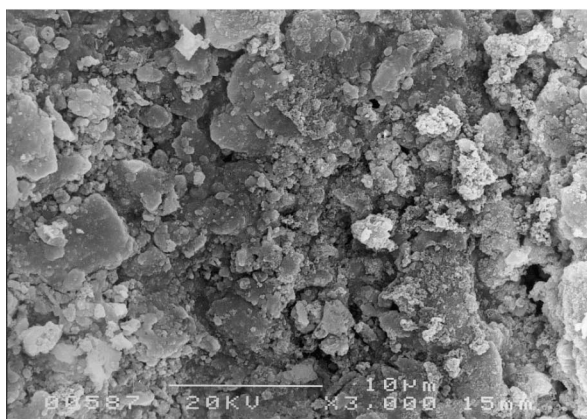
(a)
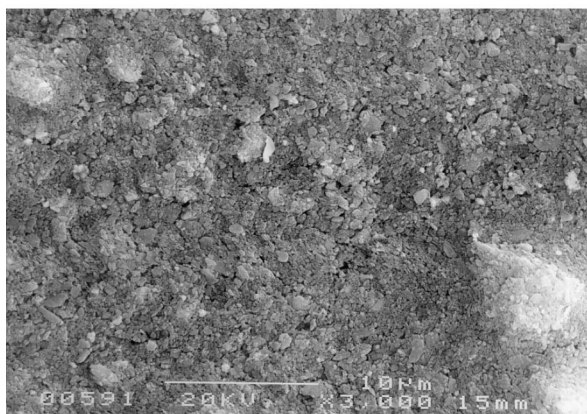
(b)

(c)

Fig. 7. Comparison (top view) of the washcoat surface: (a) commercial γ-alumina powder, $d_{90}=6$ µm (b) commercial γ-alumina powder, $d_{90}=2$ µm (c) commercial catalyst.
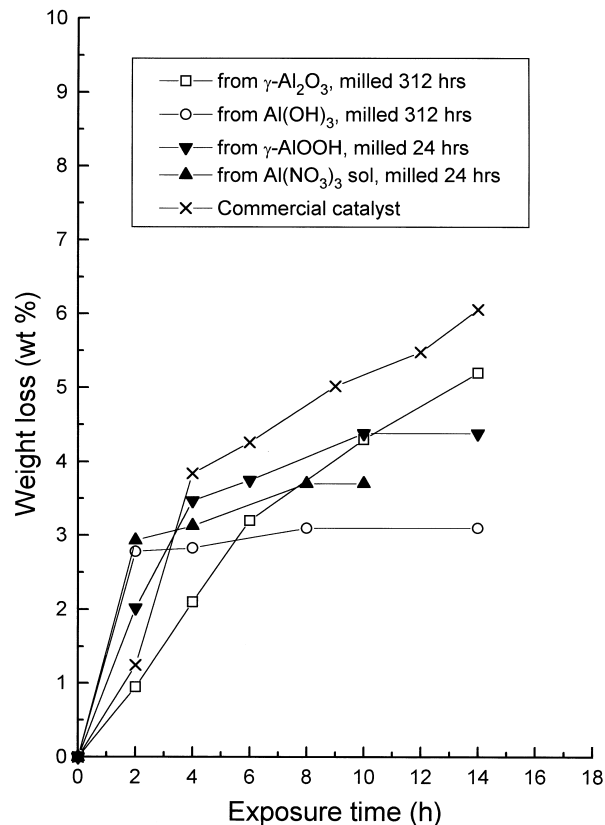

Fig. 8. Weight loss curves of γ-alumina washcoats from various precursor materials compared to that of the commercial γ-alumina powder and of a commercial catalyst.

8 and compared to these of the finer batches of the commercial γ-alumina powder and of the commercial catalyst. It can be observed that all the washcoats prepared from precursor powders exhibit less weight losses than the commercial catalyst, with the powder from $Al(OH)_3$ exhibiting the best performance. Indeed, the calcined powder from $Al(OH)_3$ not only consists of

nanoparticles but the agglomerates' size has been reduced down to the submicron range by extensive milling (Fig. 3(d)). This very fine agglomerates' size of the deposited powder from $Al(OH)_3$ can be observed in Fig. 9(a) (top view) and in (b) (substrate/washcoat interface) and compared to the respective washcoats shown in Figs. 6 and 7. The result is a very densely packed washcoat layer of uniform particle size, a fact that explains the excellent adhesion.

The respective washcoat from γ-AlOOH calcined powder is shown in Fig. 9(c) (top view) and d (substrate/washcoat interface). Even though in this case the agglomerates' size has not been reduced down to the submicron range, still their size is small enough to induce adhesion better than the commercial catalyst. This is because, as it has been already mentioned, adhesion depends both on the extent of mechanical anchorage as well as on the attractive forces exerted between the particles of the washcoat layers deposited on top of each other. Even though the larger shape of the agglomerates does not favor extensive mechanical interlocking, strong attractive forces are developed between the nanoparticles of the neighboring agglomerates, keeping the particles together. A similar situation holds for the washcoat obtained from the powder
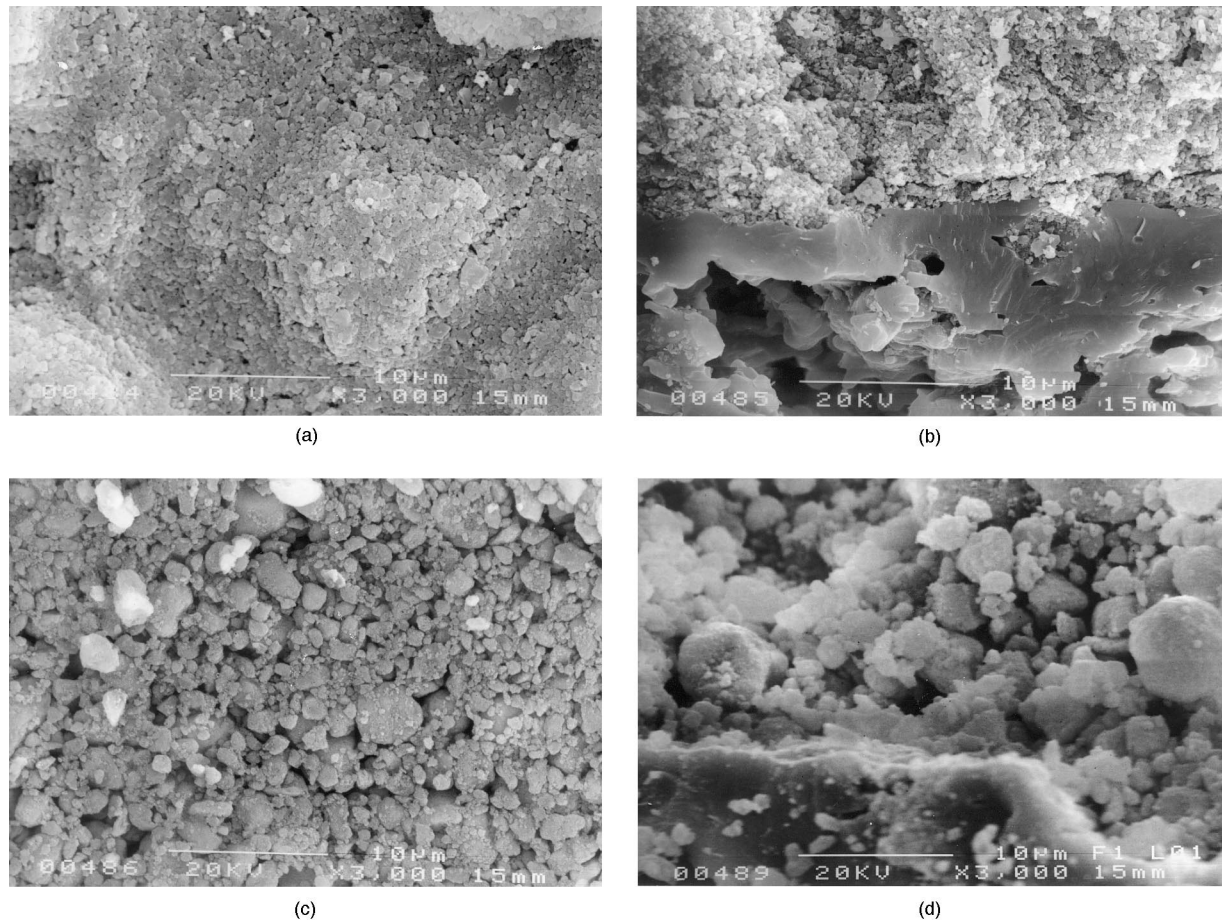
(a)

(b)

(c)

(d)

Fig. 9. Comparison of γ-alumina washcoats deposited from calcined powders from precursor materials: (a) from Al(OH)$_3$, top view, (b) from Al(OH)$_3$, substrate/washcoat interface, (c) from γ-AlOOH, top view, (d) from γ-AlOOH, substrate/washcoat interface.

produced from the calcination of the aluminum nitrate sol.

Another common characteristic shared by the washcoats produced from precursor powders is that most of their weight losses take place during a short initial period of exposure in the air stream; thereafter the weight loss curves reach a plateau value. This is in contrast to the washcoats from comercial γ-alumina which exhibit a small rise in the weight loss as a function of time (Fig. 5) and would probably experience further weight losses had their exposure in the stream of hot air been extended.

Besides reducing the washcoat particle size, in order to improve the affinity of washcoat particles with the substrate walls, chemical treatment of the support has been proposed such as "washing" of the substrates with dilute acid solutions before impregnation. This approach was tested in the present study as well, but no difference in adhesion characteristics between acid-treated and non-treated honeycombs was observed. No improvement of adhesion with chemical treatment was also observed by Cini et al.[9]

4. Conclusions

Under the severe operating conditions of automobile catalytic converters, endurance and firm adhesion of the washcoat on the substrate has to be ensured. Adhesion of the washcoat on the support takes place both by mechanical mechanisms such as "anchoring" and interlocking of the washcoat particles among them as well as with the surface irregularities of the support, and via strong interfacial forces among the powder particles. Both of these mechanisms are affected by the size of the deposited particles. In the case of dense agglomerates there exists a certain threshold value — around 5 μm — below which the agglomerates' size has to be reduced, for the achievement of satisfactory adhesion with the support. In addition, when the powder particles that comprise the agglomerates are of colloidal dimensions, adhesion is further enhanced due to the interfacial forces developed, and all of the weight losses take place in the initial stage of washcoat exposure under a hot air stream. Powders that are of colloidal size and are not agglomerated, exhibit the best adhesion and form densely

packed homogeneous layers. Further studies are under way in order to correlate the adhesion quality of various washcoats to the support properties such as porosity and pore size distribution.

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