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The effect of powder characteristics on washcoat quality. Part II: Zirconia, titania washcoats — multilayered structures

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Abstract

Novel automotive catalyst designs based on the use of washcoat systems such as yttria-stabilized zirconia (YSZ) and titania, in combination with the traditionally used γ-alumina have been recently proposed. For the development of an integrated, robust multi-layered system, good adhesion of the inner layer on the support as well as among the various layers has to be ensured. In the present work, the adhesion of zirconia and titania washcoats on cordierite honeycombs was investigated. Irrespective of the nature of the powder used, reduction of the agglomerates' size down to the order of few (2–5) microns is necessary in order to ensure firm adhesion of the washcoat to the support, comparable to that of commercial catalysts. In the deposition of multi-layered structures, particle size compatibility of the powders of the various washcoat layers can enhance the adhesion among them and induce better coherence of the overall washcoat. © 2000 Elsevier Science Ltd. All rights reserved.

Keywords: Adhesion; Catalyst supports; Membranes; Suspensions; TiO_2; ZrO_2

1. Introduction

The complete three-way automobile catalytic converter assembly, consists of three basic parts: a honeycomb ceramic support with high thermal shock resistance, a material of high surface area called the washcoat, and the catalyst species which are usually noble metals such as Pt and Rh. The cost and supply of these metals are a major drawback of these systems. A way to reduce the quantities of noble metals needed, is to enhance their catalytic activity through the exploitation of appropriate metal-support interactions. Indeed, some materials can interact with the catalyst metals, enhancing dramatically their catalytic activity. For example, strong metal-support interactions (SMSI) of titania with Rh have been observed which lead to enhanced Rh activity,[1,2] especially when the titania (rutile) lattice is doped with ions of higher valence such as W^{+6}.[2–4] On the other hand, it has been demonstrated that Pd, if properly supported on solid electrolytes with high oxygen ion conductivity such as yttria-stabilized zirconia (YSZ)[5,6] exhibits exceptional catalytic activity and can substitute a significant percentage of the more expensive Pt and Rh. Thus, multi-layered washcoat structures have been proposed, where each washcoat acts as a host for a different precious metal.[7]

It has been already mentioned that washcoat systems involve usually more than one component. For example addition of yttria is required in the case of zirconia for the formation of the oxygen-conductive cubic phase, whereas in the case of Rh supported on titania, the activity of Rh can be increased up to 20 times if the rutile lattice is doped with tungsten atoms. Wet chemistry methods such as sol–gel or coprecipitation are widely employed for the preparation of such multicomponent systems (carrier phase/additive/catalyst), since they have some inherent advantages compared to solid-state reactions. In general, wet chemistry methods lead to materials with high surface area (a desirable characteristic for automotive catalytic applications), and high activity also, the incorporation of dopants (and of the catalyst metals) can be greatly facilitated. Since the deposition of crack-free, thick coatings, upon complicated porous structures such as honeycombs, directly from the liquid phase has some inherent problems, a solution could be the preparation of powders via sol–gel

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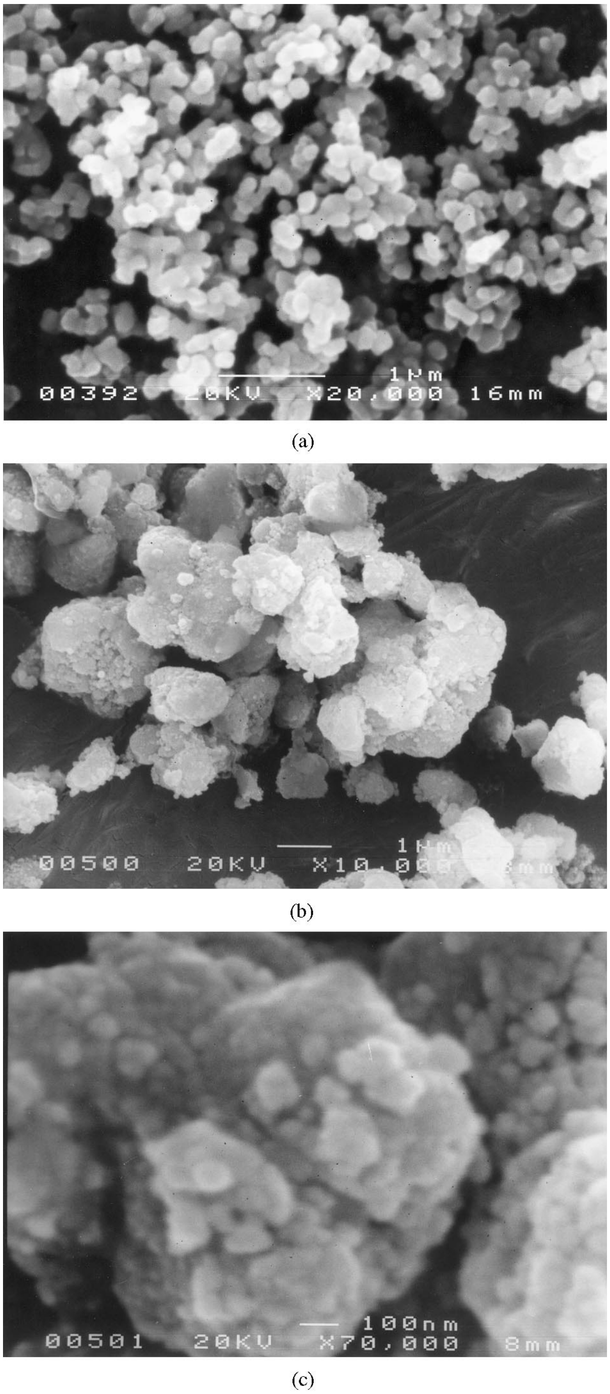
methods, the dispersion of these powders in aqueous media (preparation of slurries) and finally, their deposition upon the honeycombs.

In the case of the preparation of zirconia powders appropriate for catalytic applications, studies have been focused on the synthesis and characterization of thermally stable washcoat powders with controlled microstructure — mainly via chemical methods. Surface area loss at high temperatures seems to be the common problem of commercial monoclinic zirconia catalytic supports[8] as well as of systems prepared from gel precipitation.[9] Doping with calcia, yttria, lanthania and magnesia[10] has been employed for improvement of thermal stability but with limited success.

Titania-based systems for catalytic applications have been also synthesized by sol–gel methods with the aim to exploit the characteristics of the nanoparticles that occur from such a way of synthesis.[11–18] In general it has been found that sol–gel derived powders when dried are initially amorphous, and upon calcination they first form the metastable anatase phase. Calcination at higher temperatures has as an effect the transformation of anatase to the stable rutile phase. A much lower temperature is required for this transformation to occur for sol–gel made powders compared to conventionally-synthesized ones.[12] Doping with tungsten,[13,14] lanthanum[15] or aluminum[16] retards the anatase-to-rutile phase transformation by as much as several hundred degrees depending on the kind and the quantity of the dopant used. It has also been observed that tungsten oxide becomes segregated from the titania phase at temperatures around 900°C, before the anatase-to-rutile transformation starts.[13] Chang et al.[17] have prepared crack-free alumina, zirconia and titania membranes of thickness between 1 and 5 microns, on flat disk substrates from alkoxide solutions and characterized them with respect to pore size distribution, surface area and phase transformations upon calcination. However, all these systems exhibit the same characteristic as the zirconia ones: low surface area values especially at the temperature range of operation of an automobile catalytic converter. This surface area and porosity reduction observed in sol–gel derived nanostructured titania is attributed to the enhanced sintering during the anatase-to-rutile phase transformation.[18] Kumar et al.[18] have avoided this transformation by precipitating directly the rutile phase from a titanium isopropoxide sol by heterogeneous nucleation with the aid of Sn^{+4} ions; however the product contained about 19 mol% SnO_2. Despite the low surface area, there still exists significant interest on titania-based nanostructured catalyst systems because of the very strong metal–support interactions that noble metals such as Pt or Rh exhibit when supported on titania.

However, with the concept of multi-layered structures, the emphasis on the titania and zirconia layers, lies not so much on their high surface area but on qualities such as the SMSI of Rh with titania and the enhanced oxygen ion conductivity of the ytrria-stabilized zirconia. A high surface area of the whole structure is, of course, beneficial, but a major part of the surface area required can be provided by the contribution of the γ-alumina layer. Provided that all the qualities above are achieved, the preparation of an integrated multi-layered system with the appropriate amount of each



(a)

(b)

(c)

Fig. 1. SEM photographs of the as-received zirconia powders: (a) powder A, magnification 20 000 times; (b) powder B, magnification 10 000 times; (c) powder B, magnification 70 000 times.

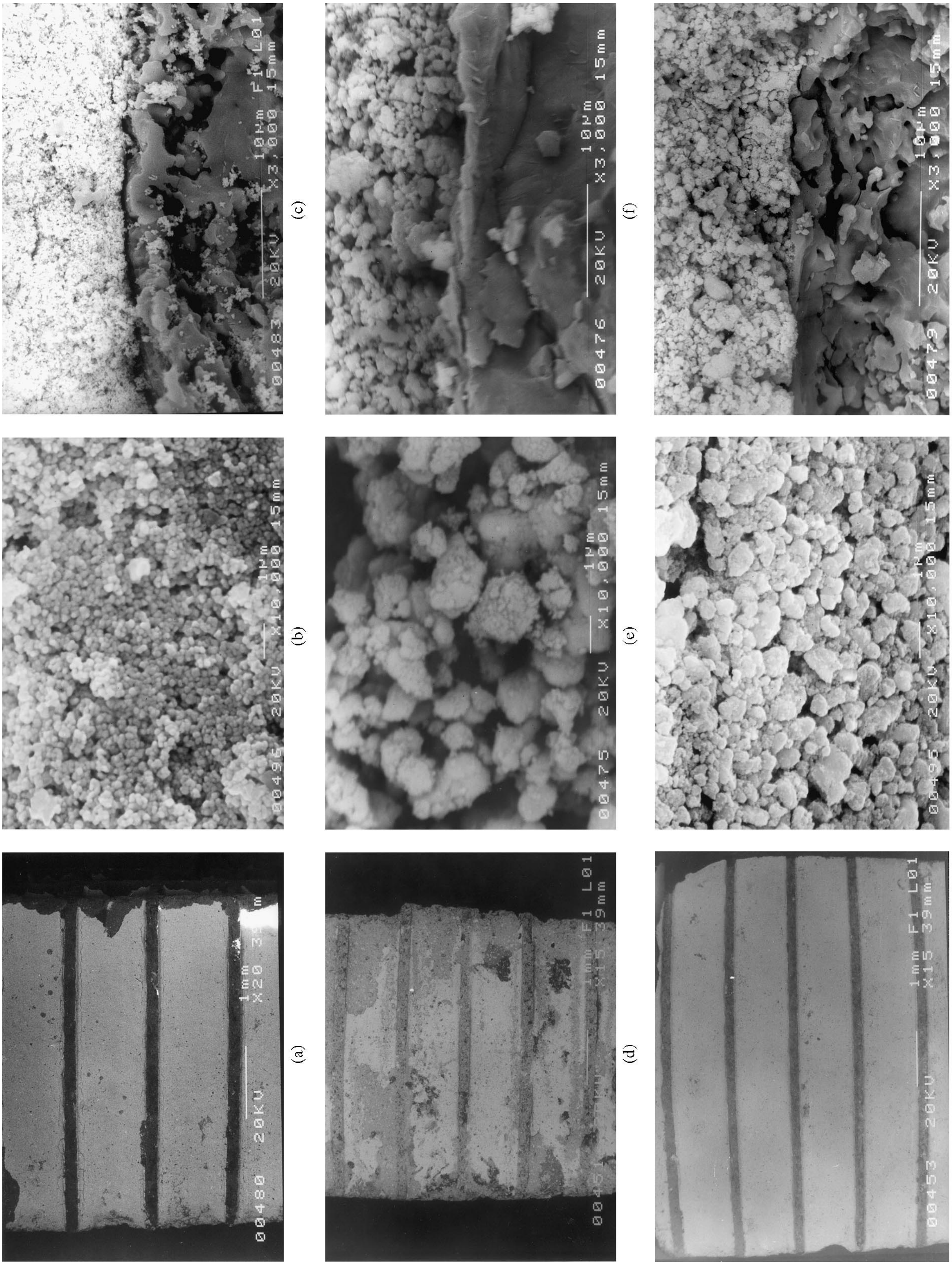


Fig. 2. Zirconia washcoats from as-received powder A [(a),(b),(c)], as-received powder B [(d),(e),(f)] and powder B milled for 72 h [(g),(h),(i)]:(a),(d) and (g) top view of coated honeycomb; (b), (e) and (h) powder deposited on the honeycomb (magnification 10 000 times); (c),(f) and (i) substrate/washcoat interface (magnification 3000 times).

washcoat has to be realized and its performance to be tested under actual automobile operation conditions, not only in terms of catalytic performance but also in terms of mechanical properties such as endurance and firm adhesion on the support.

Preliminary results on the dependence of adhesion characteristics on the powder particle size were reported in a previous work.[19] In this part of the study, the adhesion of these two kinds of washcoats, namely zirconia and titania, deposited from aqueous dispersions of powders (slurries) is investigated with the aim to correlate the coating quality to 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. Having optimized the adhesion characteristics of each particular washcoat, multi-layer structures were prepared and evaluated with respect to adhesion quality and compatibility between the various layers.

2. Experimental procedure

Two types of commercially available yttria-stabilized zirconia powders — both stabilized with 8 mol% Yttria — were employed for the preparation of zirconia washcoats, obtained from Zirconia Sales, Mandoval Ltd Surrey, UK (denoted hereafter as powder A) and Magnesium Electron Ltd Chemicals, Manchester, UK (denoted hereafter as powder B).

For the preparation of the titania washcoats, a commercial anatase powder (Merck GmbH, Darmstad, Germany) was used, which was mixed with the appropriate amount of tungsten oxide and calcined in the temperature range 900–1200°C,[7] in order to be converted to the W^{+6}-doped rutile form, which has been shown to exhibit strong metal-support interactions with Rh metal. For comparison, a powder synthesized through the sol–gel method via the hydrolysis of titanium isopropoxide with the procedure described by Lopez et al.[11] was also employed.

In a previous work,[20] the conditions for slurry stability and optimization of the deposition process for zirconia washcoats were identified. Based on these results, aqueous slurries with solids content 35 wt% were prepared and stabilized with the aid of either HCl or the ammonium salt of the poly-methacrylic acid (NH_4-PMA-commercial name Darvan C, R.T. Vanderbilt Co., Norwalk, CT). The analytical techniques (SEM, particle size analysis, X-ray diffraction) and instruments described in Part I of this work were employed for the characterization of the powders and the loaded honeycombs. The cordierite samples used for the impregnation were the same to those described in Part I, and so were the loading and calcination processes. The adhesion tests took place in the reactor described in Part I (reactor temperature = 800°C, free volume velocity = 100 000 h^{-1}).

3. Results and discussion

3.1. Zirconia washcoats

3.1.1. Powder characterization

SEM observations of the as-received powders have revealed significant morphology differences between the two types of powders used. The SEM photographs of powder A [Fig. 1(a)] indicate that the as-received powder consists essentially of discrete particles of a very fine particle size, of the order of 100–200 nm. On the contrary, particle size distribution measurements of the as-received powder B indicated a mean particle diameter of 3.1 microns, with 90% of the powders being less than 6.3 microns, in accordance to the respective SEM photographs, shown in Fig. 1(b). The as-received powder B is in the form of agglomerates, which exhibit a wide size distribution with dimensions varying from less than one to few (5–10) microns. Higher magnifications [Fig. 1(c)] revealed that these agglomerates consist also of primary units of very small dimensions, around 100 nm. However, the significant difference from powder A is that these units are strongly bound together in larger agglomerates that cannot be

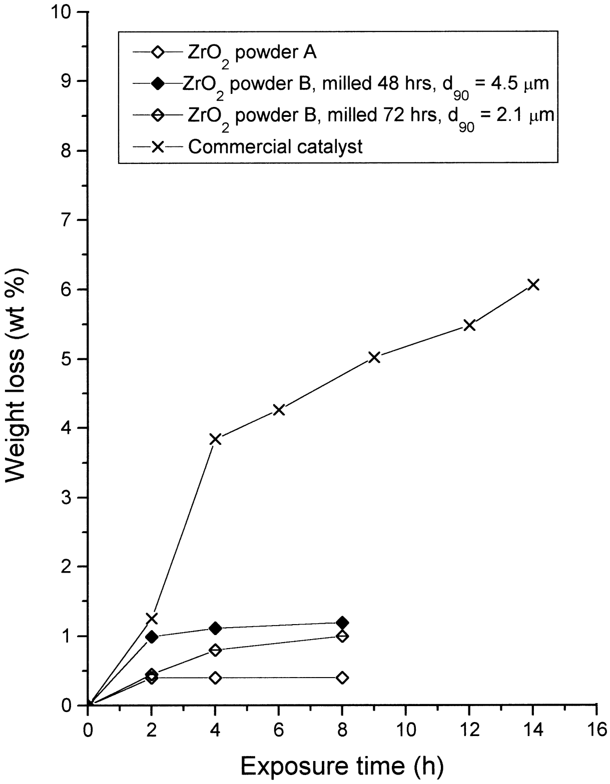


Fig. 3. Weight loss curves of various zirconia washcoats.

broken with the techniques applied during the particle size measurement (ultrasonic and mechanical stirring).

3.1.2. Adhesion studies

The first series of experiments took place with slurries that have been ball-milled for only 1 h, thus the size of the deposited particles was practically the same with that of the as-received ones. A top view of monolith channels covered with the zirconia powder A washcoat is shown in Fig. 2(a), where the uniformity of the coating can be clearly seen. The layer deposited upon the honeycomb channels (top view) is shown in Fig. 2(b) (magnification 10 000 times), where it can be seen that the particles that have covered the channel surface are indeed of very small size (100–200 nm just like the as-received ones) and exhibit a rather tight packing. The respective washcoat/substrate interface is shown in Fig. 2(c) where again the formation of a tightly-packed zirconia layer made up of very fine particles can be distinguished on the external surface of the channel. The tightness of packing due to the very fine size and uniformity of the powder deposited, can be compared to the respective photographs of the alumina washcoats in Part I of the work.

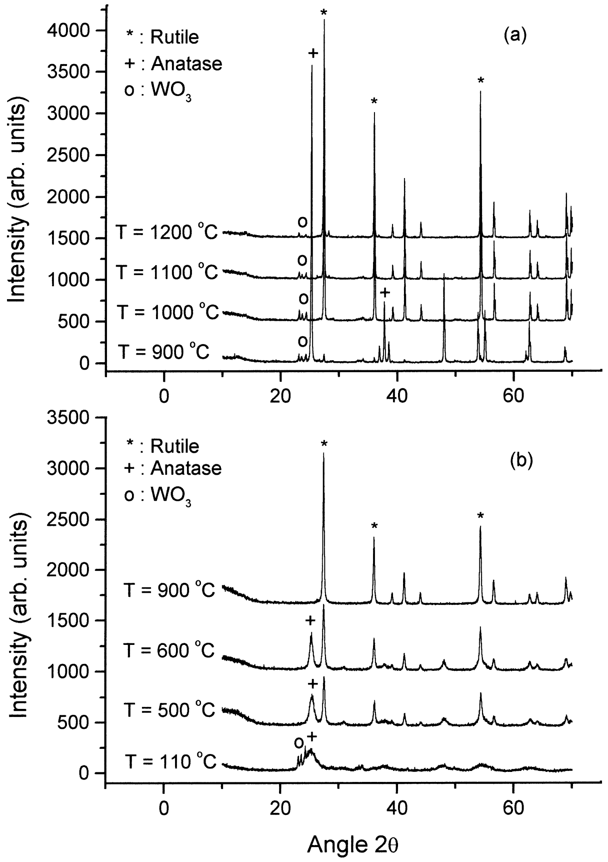
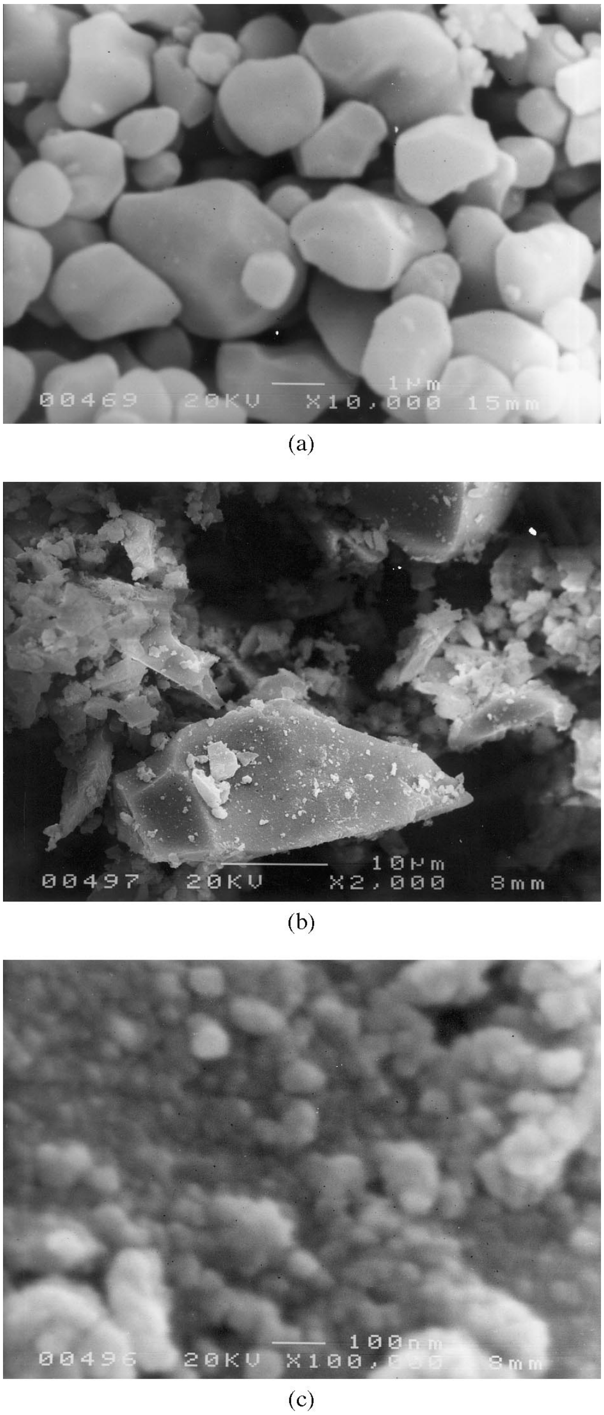


Fig. 4. Development of phase composition with calcination temperature of anatase–tungsten oxide powder mixtures: (a) commercial anatase; (b) sol–gel made anatase.

On the contrary, the as-received powder B exhibited poorer adhesion on the monolith. In Fig. 2(d), a top view of such a coated monolith is shown where the detachment of large areas of washcoat is obvious. Based on the observations on the alumina washcoats, this difference in adhesion was attributed to the much higher particle



(a)

(b)

(c)

Fig. 5. Titania powders: (a) commercial anatase powder calcined at 1200°C; (b) sol–gel made powder calcined at 600°C; (c) magnification at 100 000 times of the sol–gel made powder from (b).

size of powder B. The respective SEM photographs of powder B deposited on the honeycomb [Fig. 2(e)] and of the washcoat/substrate interface [Fig. 2(f)] indicate that the initial agglomerates remain unbroken and are deposited as such upon the monolith. The size difference between the two deposited powders [Fig. 2(b) and (e)] is obvious; so is the packing density difference between the two washcoats [Fig. 2(c) and (f)]. Compared to Fig. 2(c) (under the same magnification of 3000 times), the larger particle size of powder B results in large voids between the particles, and consequently fewer possibilities for good mechanical anchorage or interfacial interactions among them. In order to improve the adhesion of powder B, slurries were ball-milled for different periods of time up to 72 h, resulting in a drastic reduction of the characteristic diameter d_{90} from 6.5 to 1.8 microns. A monolith covered with such a slurry is shown in Fig. 2(g) where an impressive improvement of the coating quality can be observed, compared to the washcoat with the as-received powder B [Fig. 2(d)]. It should be once again mentioned here that all other deposition conditions (slurry solids content, pH, dispersant) were the same for both powders. The reduction in particle size can be clearly observed in Fig. 2(h) where particles deposited upon honeycombs for the case of 72-h ball-milling are shown and their size can be compared to that of the non-milled powder in Fig. 2(b) under the same magnification of 10 000 times. The respective substrate/washcoat interface of the washcoat from the milled powder B is shown in Fig. 2(i) [under the same magnification as Fig. 2(c) and (f)]. Reduction of particle size has resulted in a more densely packed washcoat layer with better coating quality. The particles are now much closer to one another and besides mechanical anchorage, the interfacial forces between the colloidal particles that comprise the agglomerates, enhance adhesion between them.

The dependence of the adhesion quality on the powder particle size is further reflected on the respective weight loss curves shown in Fig. 3. Powder A exhibited excellent adhesion onto the support, loosing only 0.4% of its weight after 8 h of exposure. The trend for powder B is similar to the one exhibited by the γ-alumina powder (Part I): progressive reduction of the agglomerates' size of powder B improves adhesion quality and eventually results in a performance much better than that of a commercial catalyst. However, the best performance in terms of adhesion is exhibited by powder A, a fact that can be attributed to the very fine particle size of the deposited powder. All the washcoats exhibit the same trend as the ones from alumina materials that are comprised of nanoparticles: levelling off of the weight loss curves after a very short period.

3.2. Titania washcoats

In the Introduction, it was mentioned that one way to enhance metal-support interactions is to dope the titania lattice with W^{+6} ions.[2,3] This doping can be achieved by mixing the anatase powder with the appropriate amount of tungsten oxide and subsequent calcination. The calcination temperature has to be high enough so that two phenomena can take place: transformation of the anatase to rutile and diffusion of the W^{+6} ions into the rutile lattice for the formation of a solid solution. The development of phase composition with calcination temperature of a commercial anatase–tungsten oxide powder mixture is shown in Fig. 4(a). First of all it can

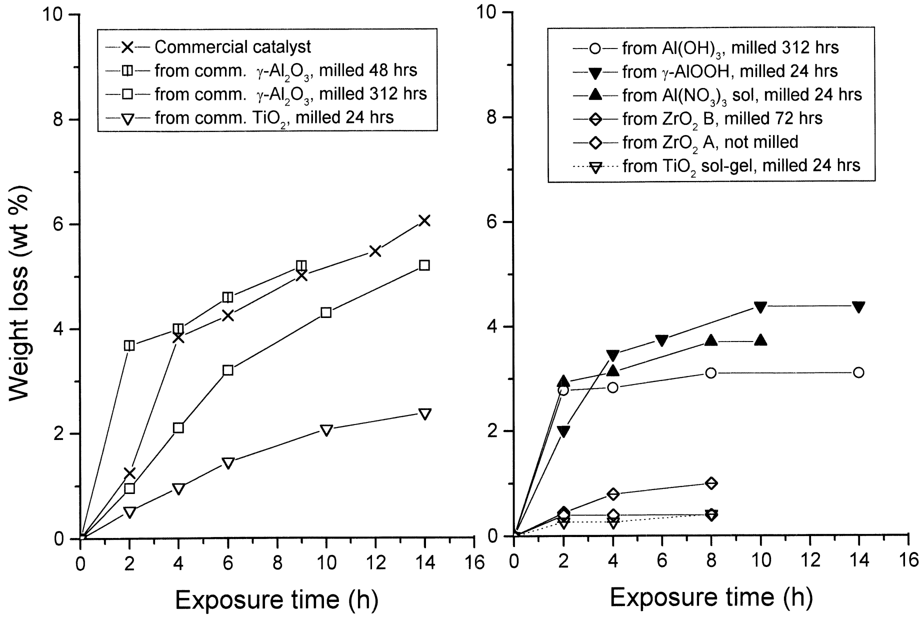
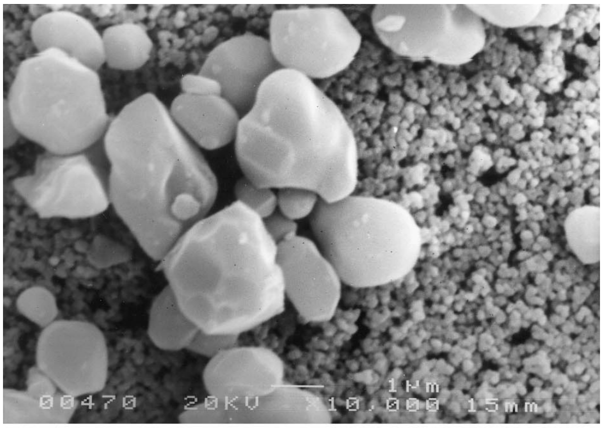


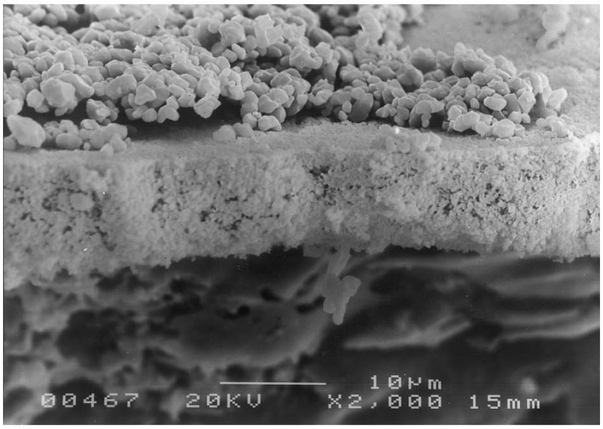
Fig. 6. Weight loss curves of washcoats from various fine powders compared to that of a commercial catalyst.

be observed that a calcination temperature of 1000°C is required for the anatase-to-rutile transformation to take place. However, even at this high temperature still the tungsten oxide remains as a separate phase. The calcination temperature required for the completion of the diffusion of the tungsten ions into the rutile lattice and the disappearance of the X-ray diffraction peaks corresponding to tungsten oxide is as high as 1200°C. The phase development of the mixture of a dried, sol–gel produced anatase powder with the same amount of tungsten oxide is shown in Fig. 4(b). The X-ray diagram of the mixture of the powder produced after drying of the gel at 110°C with tungsten oxide, shows the peaks of poorly crystallized anatase together with the tungsten oxide peaks. At a calcination temperature of 500°C anatase has already been partially crystallized to rutile and the tungsten oxide peaks have disappeared. As the calcination temperature is increased the anatase-to-rutile transformation proceeds to completion. At 900°C, only the rutile peaks are present, a fact that indicates the formation of the tungsten-doped rutile phase.

The high calcination temperatures required in the case of commercial anatase, have as a result an increase of the particle size of the product. Particle size measurements of the calcined titania powder (after a short milling time of 24 h) indicated a characteristic particle diameter of 1.8 microns, in accordance with the relevant SEM observations [Fig. 5(a)]. From Fig. 5(a) it is also evident that the tungsten-doped rutile powder consists



(a)



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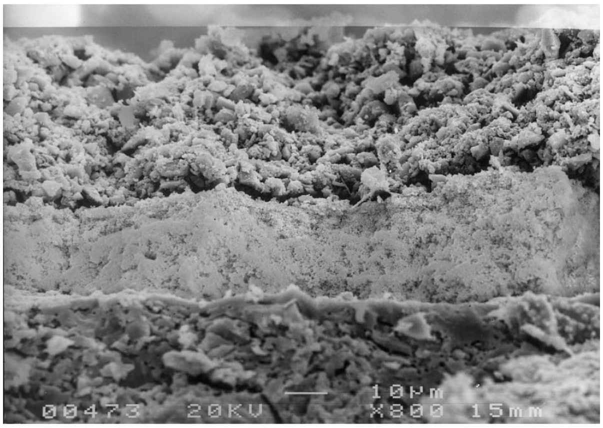
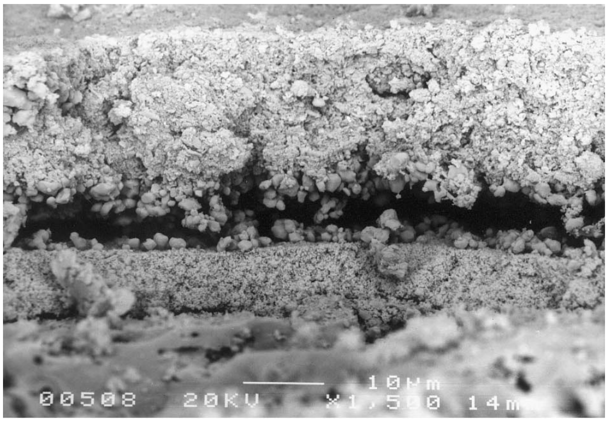
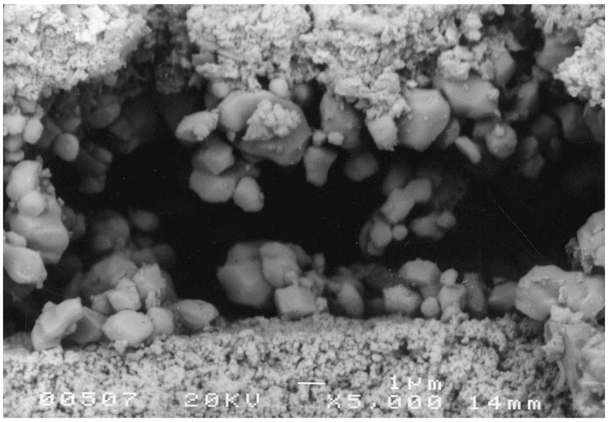


(c)

Fig. 7. Two-layered zirconia/titania washcoats: (a) commercial titania powder, top view; (b) commercial titania powder, substrate/washcoat interface; (c) sol–gel made titania powder, substrate/washcoat interface.



(a)



(b)

Fig. 8. Three-layered washcoats with: intermediate layer of commercial titania; (a) magnification 1500 times; (b) magnification 5000 times.

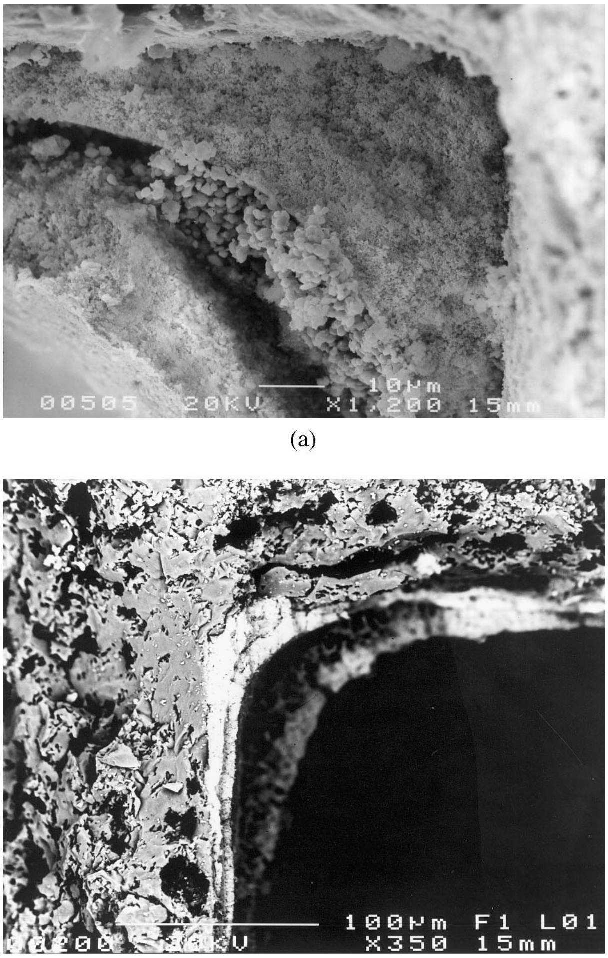
of dense, quasi-spherical grains with relatively uniform particle size distribution. On the contrary, in the case of sol–gel powders the low calcination temperature does not favor the sintering of the titania crystallites and the formation of dense particles. Even though the sol–gel made powder after calcination has the form of agglomerates of irregular shape and of a wide size distribution [Fig. 5(b)], large magnifications [100 000 times; Fig. 5(c)], reveal the very fine size of the titania crystallites which are less than 100 nm in contrast to the dense particles of commercial calcined titania.

The weight losses of the two titania washcoats are plotted in Fig. 6. together with the respective weight losses of other representative washcoats of alumina and zirconia. In Fig. 6(a) the weight loss curves of washcoats deposited from commercial powders with dimensions of a few microns are shown, whereas in Fig. 6(b) the respective curves from powders that consist of nanoparticles are presented. As far as the titania washcoats are concerned the better adhesion of the sol–gel made powder is evident.

Some general conclusions can also be drawn. The two categories of powders exhibit a different trend: for the case of nanoparticles the weight losses are practically completed within a short initial time period and the relevant curves reach a plateau value. The respective curves of the commercial powders show an increasing trend: it is evident that further weight losses should be expected at longer exposure times. Irrespective of the nature of the powder used, there exists a general trend: when the deposited powder is in the form of agglomerates, progressive reduction of the agglomerates' size (e.g. by extensive milling) improves the adhesion of the washcoat on the support and eventual reduction below a certain threshold value (around 5 microns) is required in order to ensure adhesion better than that of commercial washcoats. This trend has been observed for both, commercial alumina and zirconia powders. If, in addition, these agglomerates consist of nanoparticles, denser washcoat layers with better adhesion are formed. This is because, when the size of these nanoparticle agglomerates is reduced below a certain value, better contact among the agglomerates is obtained and strong interfacial forces between the nanoparticles are acting in combination with mechanical anchorage mechanisms. The most favorable case is when the powders to be used are of nanophase dimensions and show no tendency to form large, hard agglomerates, such as in the case of the commercial zirconia powder A. These kinds of powders form very tightly packed washoat layers, with excellent adhesion, suffering only from minor weight losses, which in addition are completed within a very short period.

3.3. Multi-layered washcoats

The above results were used for the deposition of multilayered washcoats. The proposed configuration is an inner layer of zirconia, an intermediate layer of titania and an outer layer of γ-alumina.[6] Zirconia of powder A was used as the innermost layer because it exhibited the best adhesion on the cordierite support among the various zirconia powders. Upon this layer the two kinds of tungsten-doped titania powder (commercial and sol–gel made) were deposited. In Fig. 7(a) a washcoat layer from the commercial titania deposited on a zirconia layer of powder A is shown (top view). The size mismatch between the two powders is obvious — and leads to a very poor adhesion between the two layers with clearly visible gaps [Fig. 7(b)]. The titania particles are practically just spread on the zirconia ones; due to the very large size mismatch, neither mechanical interlocking between the two kinds of powders can take place, nor the development of strong interfacial forces adequate to adhere the coarser titania powders onto the much finer zirconia ones, is possible. The thickness of the titania washcoat is also limited to very few (one to two) layers of titania particles. In contrast, the sol-gel made powder deposited on the same zirconia



(a)

(b)

Fig. 9. Comparison between three-layered catalysts: (a) intermediate layer of commercial titania; (b) intermediate layer of sol–gel titania.

layer exhibits a different picture [Fig. 7(c)]. Provided that the agglomerates' size has been reduced around 2 microns, a thick, tightly packed layer of titania has been deposited uniformly upon the zirconia layer.

The effect on adhesion can be clearly seen on the photographs of three-layered washcoats where the intermediate layer is from commercial titania, shown in Fig. 8a and b. In this case due to the large size mismatch between titania and zirconia, a multi-layer structure of very poor quality is obtained, where large gaps between the zirconia and the alumina layer can be clearly observed. The titania particles are so weakly adhered onto the zirconia layer underneath, that a great percentage of them gets removed during the next impregnation with the alumina slurry; the titania layer can be barely seen between the zirconia and the alumina layers. In larger magnifications [Fig. 8(b)], the few titania particles badly adhered to either the zirconia or the alumina layer can be clearly observed, as well as the gap between the innermost and the outmost layer. The alumina layer is practically not attached at all on the zirconia one.

In Fig. 9(a) and (b), two three-layered structures, one with an intermediate layer from commercial titania [Fig. 9(a)] and one with an intermediate layer of sol–gel made one, are compared. A much thicker, clearly visible titania layer, is deposited from the sol–gel made powder which in addition is much better adhered to both the zirconia layer underneath and the alumina layer on top.

4. Conclusions

For the preparation of integrated multi-layered washcoat systems appropriate for automotive catalytic applications, firm adhesion among the layers as well as with the support has to be ensured. Adhesion quality depends on the particle size of the deposited powders. This dependence on particle size seems to be general, irrespective of the kind of powder employed. If the powder to be deposited is agglomerated, reduction of the agglomerates' size below a certain threshold value — around 5 microns — is required in order to ensure firm adhesion of the innermost zirconia layer on the cordierite support. On the contrary, powders that are of colloidal size and are not agglomerated, exhibit excellent adhesion with the support and form densely packed homogeneous layers. In the case of multi-layered washcoats, size compatibility among the various kinds of deposited powders is necessary for the achievement of strong adhesion between the various layers and deposition of an adequate amount of each washcoat layer. Powders synthesized from wet chemistry methods seem to exhibit advantages such as lower calcination temperatures required for the formation of the desired doped phases and thus smaller grain size which induces better adhesion. Further comparisons with respect to thermal stability and catalytic activity are under way in order to identify the best synthesis routes for the design of multi-layered three-way automobile catalysts.

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