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The effect of processing parameters on the properties of γ-alumina washcoats deposited on ceramic honeycombs

C. AGRAFIOTIS, A. TSETSEKOU
Ceramics and Refractories Technological Development Company, (Cereco S.A.),
72nd km of Athens—Lamia Ntl. Road, P.O. Box 146, 34100, Chalkida, Greece
E-mail: athtse@hotmail.com

The coating of cordierite honeycomb specimens with γ-alumina slurries for the preparation of washcoats for automotive applications was investigated. The dependence of slurry viscosity on factors such as the solids content, the pH and the particle size distribution of the powder used, was determined. Slurry viscosity was correlated to the loading percentage achieved, as well as to the quality of the washcoat in terms of homogeneity and reproducibility. It was found than an adequate solids content in the slurry is necessary for the achievement of satisfactory loading per impregnation. When, though, the particle size of the powder employed is of colloidal dimensions, high solids content leads to extremely high viscosity values. Adjustment of the slurry viscosity is therefore necessary and this was achieved with the use of either HCl or ammonium poly-methacrylate, an organic polyelectrolyte. Optimum loading conditions were achieved when the slurry viscosity lied between 50–150 mPa·s. For a specific solids content, the organic polyelectrolyte led to lower viscosity slurries and resulted in better reproducibility of the loading percentage. With the use of ammonium poly-methacrylate, slurries of fine particles, up to 40 wt % solids content could be handled, resulting in reproducible loading percentages of the order of 15 wt %.

1. Introduction

The complete automobile catalytic converter assembly is comprised of three basic parts. The first one is the substrate, which in most of the cases is a ceramic thin-walled honeycomb structure. The interior walls of this substrate are coated with a layer of a high surface area material—called the washcoat. Finally, within the matrix of the washcoat, the noble metals that catalyze the conversion reactions of the noxious emission gases to harmless ones, are dispersed. The washcoat material should possess a variety of properties such as high surface area, appropriate pore structure and thermal stability. A material that combines these properties and is mostly used in these applications is γ-alumina.

The washcoat is usually applied on the honeycomb by the impregnation of the substrate in a γ-alumina slurry [1, 2]. Removal of the excess slurry from the substrate channels, drying and subsequent calcination are employed for the formation of a solid washcoat layer on the honeycomb walls. Instead of the calcined γ-alumina form, dispersible precursor powders such as boehmite (γ-AlOOH) are often used [3]. Impregnation of the honeycombs with boehmite slurries takes place and the coated monolith is then calcined around 600 °C where the transformation of the precursor material to γ-alumina takes place upon the monolith. Another method for the coating of substrates is the Sol-Gel method where, instead of powders, liquid precursor materials (sols) are used. The substrate is immersed in the precursor sol, and during the following drying and calcination steps the sol forms a gel-like layer upon the substrate. This method is widely used for the preparation of membranes on ceramic substrates of various geometries such as discs [4], cylinders and honeycombs [5, 6].

The ultimate goal of the deposition process is the loading of the honeycomb with a predetermined amount of washcoat in the form of a homogeneous layer, strongly adhered onto the monolith walls. For the coating process to be efficient, precise adjustment of the slurry characteristics such as the solids content, the slurry viscosity and the pH, is needed. Even though a lot of work has been devoted to the synthesis of thermally stable washcoat powders, little emphasis has been given on the preparation of stable slurries of these powders, optimization of the slurry properties and on the coating of honeycombs with such slurries. In particular, correlations between the slurry properties and the coating process in terms of efficiency and coating quality are very sparse in the literature.

Blachou *et al.* [1], used a γ-alumina powder which was the product of calcination of gibbsite ($Al(OH)_3$) at 600 °C for 3 hours. They reduced the powders' particle size down to 3.3 μm by ball-milling with the addition of HCl and they studied the effect of HCl concentration on slurry viscosity. They observed a strong dependence of slurry viscosity on pH and a transition to high viscosity behaviour when a certain pH value was exceeded. This pH value is lower as the solids content of the slurry is increased. They recommended a slurry with 42 wt % solids content and a pH of 3.7, with which a total loading of 18–22 wt % was achieved with two impregnations. Even though they have used different particle size distributions, they did not study the effect of particle size on slurry viscosity, loading percentage and coating quality. This viscosity dependence on pH and the transition to a region of extremely high viscosity at a pH value which depends on the solids content of the slurry has been also observed for slurries of other ceramic powders such as a-alumina and zirconia [7].

Instead of the typical impregnation technique, Shimrock *et al*. [2] applied vacuum in order to draw a predetermined amount of alumina slurry into the interior of honeycombs. They suggested a slurry solids content between 35–52 wt % and control of the slurry viscosity between 15–300 mPa·s; under these conditions uniform loading could be achieved. However there is no mention of either the slurry pH or of the particle size of the alumina powder used.

Stabilization of ceramic slurries, especially at high solids content is often achieved with the addition of organic polyelectrolytes. These act with a combined electrostatic and steric effect keeping the particles apart so that they do not flocculate and settle under the effect of gravity. Even though they have found extensive use in the stabilization of ceramic slurries for applications such as slip-casting and spray-drying, they have not been used for the preparation of slurries for washcoating processes. One of the most efficient of these deflocculants is the ammonium salt of the polymethacrylic acid (ammonium poly-methacrylate—NH_4-PMA) known with the commercial name of Darvan C*. The action of this deflocculant has been studied a lot, in particular in the stabilization of colloidal a-alumina slurries [8–10]. Corradi *et al*. [11] have tested polyelectrolyte stabilization in slurries of ceramic clays, in order to avoid problems related to high viscosity, aging and processing of multiphase systems, present in electrostatically stabilized systems. They have found indeed that sodium polymethacrylates could be successfully used for the stabilization of clay slurries.

The effect of particle size on slurry characteristics was studied by Tari *et al*. [12] who blended two commercial a-alumina powders with different particle size distributions. They observed, that for the same solids content, slurries containing higher proportions of the coarser particles exhibited lower viscosity values. They suggest that a bimodal particle size can lead to a more effective particle packing and to stable slurries of high solids content (up to 70 vl %) and relatively low viscosity.

In the present work we have tried to optimize the coating process correlating the rheological properties of γ-alumina slurries to the loading characteristics of the honeycomb substrates. Properties, such as the stability and the viscosity of the slurry, the kind of the deflocculant used and the particle size of the powder, were correlated not only to the quantitative characteristics of the loading process, but also to the quality of the coating in terms of morphology and reproducibility. Emphasis was placed on the stabilization of slurries with organic deflocculants—an approach very popular in ceramic processing, but not tested upon the preparation of slurries for the coating of complicated structures such as honeycombs.

2. Experimental

The raw alumina material employed was powder of γ-Al_2O_3 (Pechiney, Greece) which is a by-product of the Bayer process. The powder was ball-milled with alumina grinding media in order to obtain fractions of various mean particle diameters. Particle size distributions were measured with the aid of a laser particle size analyzer (Malvern E-3600).

The powders with the desired particle size distribution were mixed with the necessary amount of water and the slurry was ball-milled with alumina grinding media, for one hour. When adjustment of the pH or of the viscosity of the slurry was necessary, the appropriate amount of acid (HCl), base (NaOH), or deflocculant was added and the slurry was conditioned by stirring for 2 hours. The deflocculant used was the ammonium salt of the polymethacrylic acid (NH_4-PMA).

The stability of the slurries was studied with the aid of zeta-potential measurements in a MALVERN Zetasizer 2000 instrument. Small samples from slurries were diluted in aqueous solutions of 0.001 M NaCl. Samples of the solutions were injected in the electrophoresis cell and the average value of four samples and two measurements per sample was obtained. The pH was adjusted with either HCl or NaOH 0.1 M solutions. In order to study the effect of deflocculant, slurries with the same solids content, but with the addition of NH_4-PMA were prepared and the same procedure was followed thereafter.

Slurry viscosities were measured with the aid of a Brookfield Viscometer (model RVT DV-II) with the HV spindle set. Sets of measurements with a specific spindle were taken, at all shear rates where a reading of the viscosity value could be obtained.

The impregnation procedure was as follows: cylindrical cordierite samples manufactured by CERECO, with 400 square cells/in^2 were immersed in the slurry, which was under stirring, for one minute. In most of the experiments five specimens of 1.5 cm diameter and 2 cm length were employed. 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 one and a half hours and calcined at 600 °C for two hours. Loading percentage was determined from the increase of specimen weight.

The morphology of the starting powders as well as of the coated honeycombs (homogeneity and microstructure of the coatings) was studied with the aid of a JEOL-6300 Scanning Electron Microscope.

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* R. T. Vanderbilt Co., Norwalk, CT, USA.

3. Results

3.1. Particle size reduction—morphology

Particle size analysis measurements 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 microns. Typical SEM photographs of the powder are shown in Fig. 1a. It can be clearly seen that the particles of the as-received powder have diameters of few tens of microns, are of uniform size and they are essentially agglomerates consisting of smaller units. Reduction of the initial particle diameter (d_{90}) of 52 microns down to 6 microns was achieved within 48 hours of ball-milling; however, for 90% of the powder to become less than 2 microns an extensive milling time of 312 hours was required. SEM photographs of batches with $d_{90} = 6$ and $d_{90} = 2$ μm are shown in Fig. 1b and c respectively. A wide size distribution, where agglomerates of irregular shape and of a size of few microns coexist with many smaller particles with diameters much less than 1 micron can be observed.

3.2. Slurry stability

The stability of the slurry was studied with the aid of zeta-potential measurements. The dependence of zeta-potential on slurry pH and on deflocculant concentration is depicted in Fig. 2a and b respectively. In the absence of deflocculant (Fig. 2a, solid line) the isoelectric point of γ-alumina occurred around 7.7, whereas high values of zeta-potential and therefore good dispersion were achieved at pH values lower than 5 or greater than 9. With the addition of 1 wt % deflocculant (Fig. 2a, dotted line) the whole zeta-potential—pH curve is shifted towards a lower pH region and the isoelectric point of the slurry to pH 5.5. Large values of zeta-potential (greater than 40 mV) are observed at pHs higher than 7.5 and the slurry is now well dispersed in a much wider pH range (from 7.5 to 9.5).

The effect of NH_4-PMA concentration on the slurry zeta-potential is shown in Fig. 2b. The solid line corresponds to pH $= 9.5$ (the natural pH of the slurry) whereas the dotted line to pH $= 6.6$, which is the "natural" pH of the 0.001 M NaCl solution and lies in a pH region where the alumina slurry is flocculated (Fig. 2a). In the first case, the variation in zeta-potential with the addition of NH_4-PMA is not large; nevertheless, deflocculant helps in increasing the zeta-potential, which achieves its plateau value of -40 mV for a deflocculant concentration of 1 wt %. For the second case, the effect of NH_4-PMA concentration is much more prominent: small quantities of NH_4-PMA are not sufficient for deflocculation. A significantly larger addition of NH_4-PMA (more than 2 wt %) is required in order to deflocculate the slurry and achieve the plateau zeta-potential value.

3.3. Effect of solids content, powder particle size and deflocculant addition on slurry viscosity

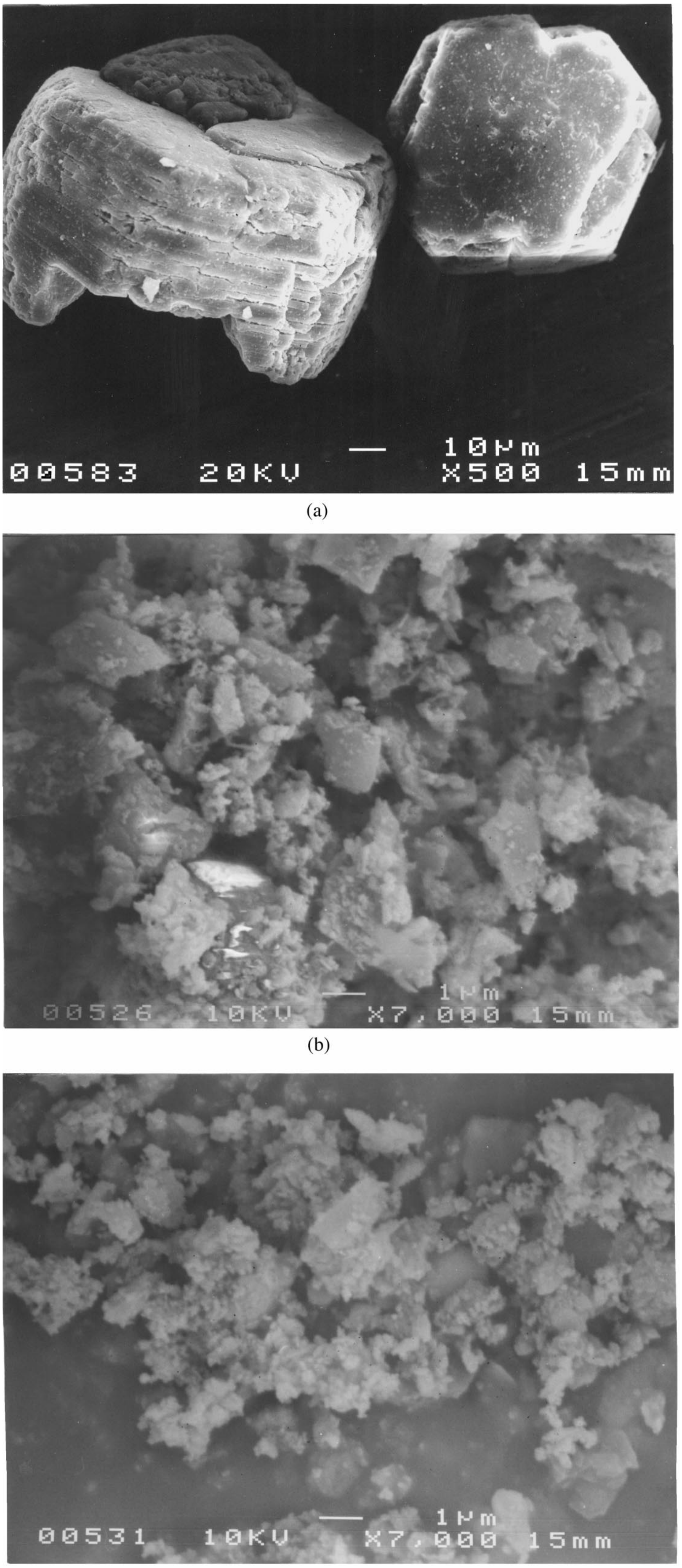
Slurry stability is affected from the particle size of the powder used. Particles coarser than 6 microns had a tendency to settle fast, not only making impossible any viscosity measurements but also requiring vigorous stirring for the homogenization of the slurries during the impregnation process. Thus, powder batches of $d_{90} = 6$ μm and $d_{90} = 2$ μm were employed for the loading experiments, with solids content of 30, 35, 40 and 45 wt %. Based on the results above, two sets of slurries were prepared for each case: one with the addition of HCl until pH $= 4.0$ and another one with the addition of 1 wt % NH_4-PMA and a pH around 9.5.

Typical viscosity-shear rate curves are shown in Fig. 3 for the case of the finest alumina used. All slurries studied were pseudo-plastic, i.e. viscosity decreased with increasing shear rate. As the solids content in the slurry increases, viscosity also increases: for solids content greater than 40 wt % viscosity becomes much greater, requiring another spindle in order to be measured. Similar rheological behaviour was observed for slurries stabilized with NH_4-PMA, as well as with the slurries of the coarser particles ($d_{90} = 6$ μm).

The dependence of viscosity on the solids content, and on the nature of the deflocculant used is given in Fig. 4 for slurries of both the coarser and the finer particles. In this graph and hereafter, the minimum viscosity value is taken into account (i.e. the one obtained at the maximum shear rate for the specific slurry). For the coarser particles and in the range of solids content examined (30–45 wt %), viscosity increases almost linearly with solids content. On the contrary, for the finer particles, viscosity varies exponentially with solids content: an increase on the solids content by 5 wt % almost doubles the slurry viscosity, which at 45 wt % solids content, has become more than 300 mPa·s. The effect of deflocculant is minimal at low solids content: for both powder particle sizes tested, slurries with NH_4-PMA exhibit viscosity values only slightly lower than slurries with HCl. However, as the solids content of the slurry is increased, the beneficial effect of NH_4-PMA in reducing the slurry viscosity can be clearly observed. For a specific solids content and powder particle size, slurries with NH_4-PMA are always less viscous than the respective slurries with HCl, this effect being much more prominent in the case of slurries of coarser particles.

3.4. Effect of slurry solids content on loading percentage

This viscosity dependence on powder particle size and solids content, is reflected upon the percentage of loading achieved per impregnation. The variation of the loading percentage with solids content is shown in Fig. 5a and b for the cases of $d_{90} = 6$ μm and $d_{90} = 2$ μm, respectively. In these graphs the loading percentages achieved in all honeycomb samples tested per experiment are compared, in order to visualize the reproducibility of the loading process. The lines pass through the average values of loading percentage at each solids content. For both particle size distributions, loading is low at low solids content and increases progressively as the solids content in the slurry is increased. Increasing the slurry solids content from 30 to 45 wt % results in



(a)

(b)

(c)

Figure 1 SEM photographs of the γ-alumina powder: (a) As-received, (b) ball-milled for 48 hrs, $d_{90} = 6\ \mu$m, (c) ball-milled for 312 hrs, $d_{90} = 2\ \mu$m.

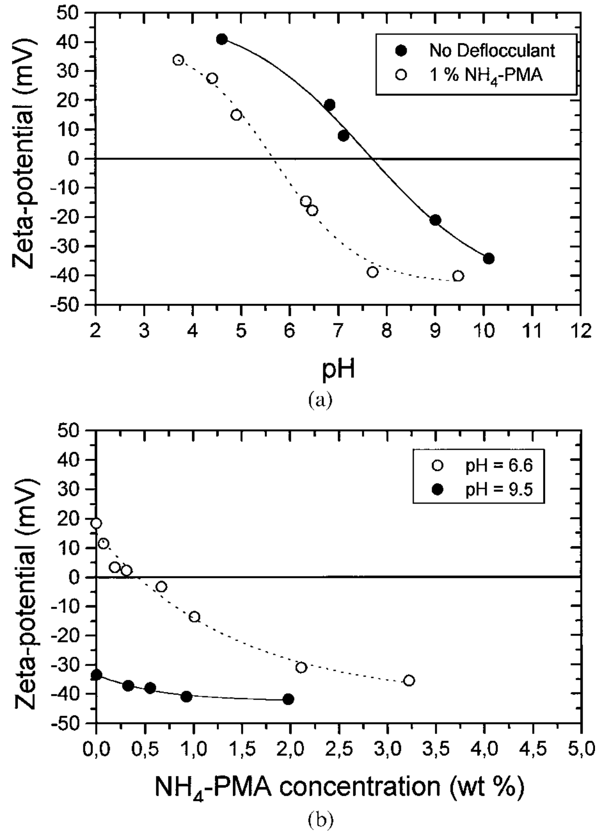


Figure 2 Zeta—potential of γ-alumina slurries as a function of: (a) pH and (b) deflocculant concentration.

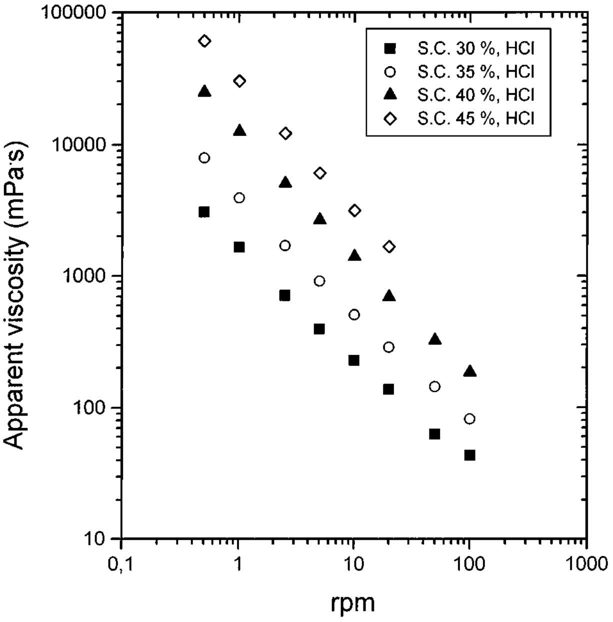


Figure 3 Slurry viscosity as a function of shear rate and solids content for slurries of powder with $d_{90} = 2\ \mu$m, dispersed with HCl.

an almost four-fold increase on the loading percentage achieved. Loading percentage depends also on the use of deflocculant and on the powder particle size, since these two factors affect the slurry viscosity.

Addition of deflocculant improves the reproducibility of the loading achieved from sample to sample. As it can be observed in Fig. 5a and b, the use of NH_4-PMA compared to HCl, allows, in general, for better reproducibility of the loading percentages achieved among the samples, for both the particle size distributions used. This is especially true for the high solids content slurries (45 wt %). At these high solids content values, even though the loading percentage lies in the range 20–25 wt %, in the absence of deflocculant poor reproducibility of the loading percentage among

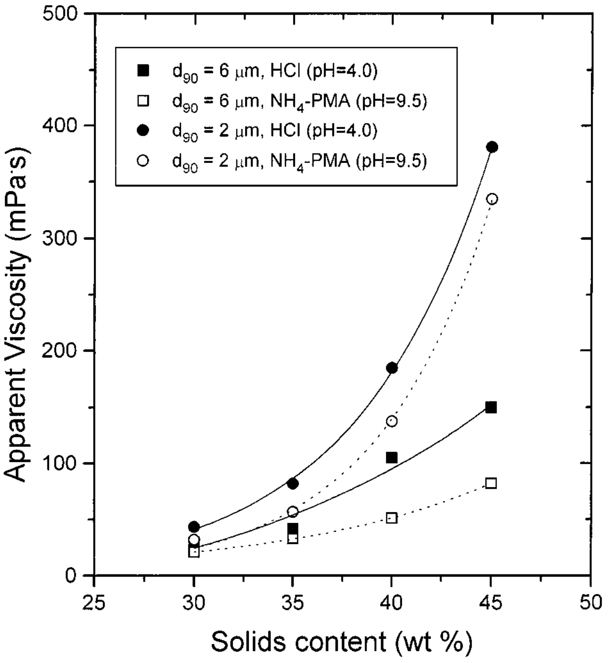


Figure 4 Slurry viscosity as a function of solids content, powder particle size and deflocculant used.

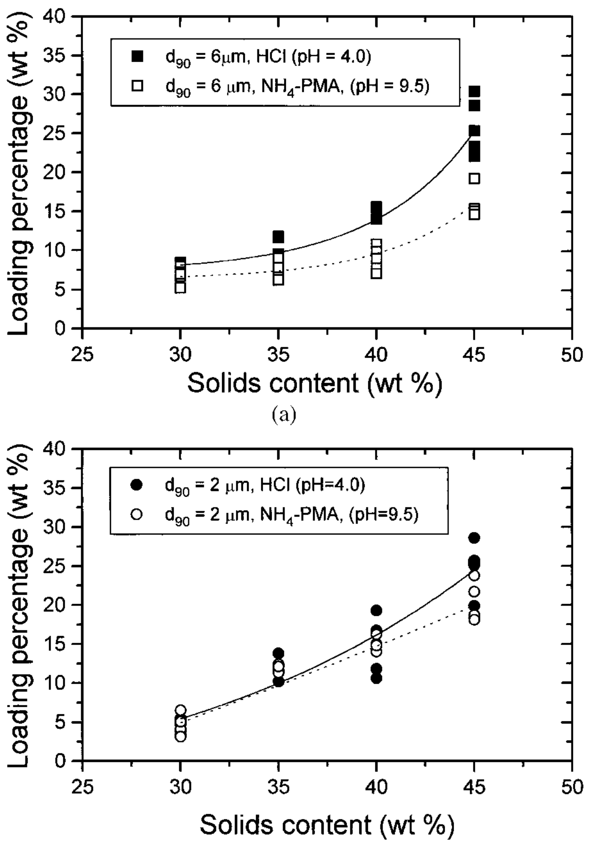


Figure 5 Loading percentage achieved as a function of slurry solids content and deflocculant used: (a) Powder of $d_{90} = 6\ \mu$m, (b) powder of $d_{90} = 2\ \mu$m.

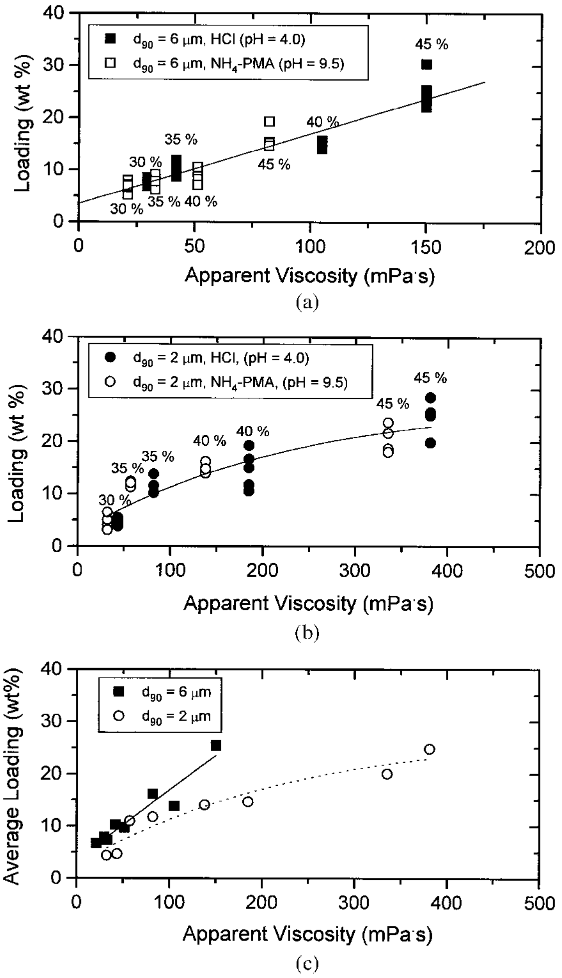


Figure 6 Loading percentage achieved as a function of slurry viscosity and deflocculant used: (a) Powder of $d_{90} = 6$ μm, (b) powder of $d_{90} = 2$ μm, (c) average loading percentage achieved for both powders.

the samples is observed: the variation in loading among samples impregnated in the same slurry can be as high as 50%.

3.5. Effect of slurry viscosity on loading percentage

The results above can be summarized in a plot of loading percentage achieved vs. slurry viscosity. These plots are shown in Fig. 6a and b for the two particle size distributions used. The viscosity-loading trend is similar for both deflocculants (NH$_4$-PMA and HCl), for each particle size employed. Irrespective of the deflocculant used, loading percentage seems to vary proportionally with slurry viscosity for the case of coarser particles, whereas for the case of finer particles, the trend is described from a parabolic line. Therefore, the loading percentage—viscosity trend can be summarized in a plot like the one in Fig. 6c for all the slurries employed. The curves for the slurries with the two different particle size distributions are plotted separately, whereas on each curve the points with the use of both deflocculants (HCl and NH$_4$-PMA) are included.

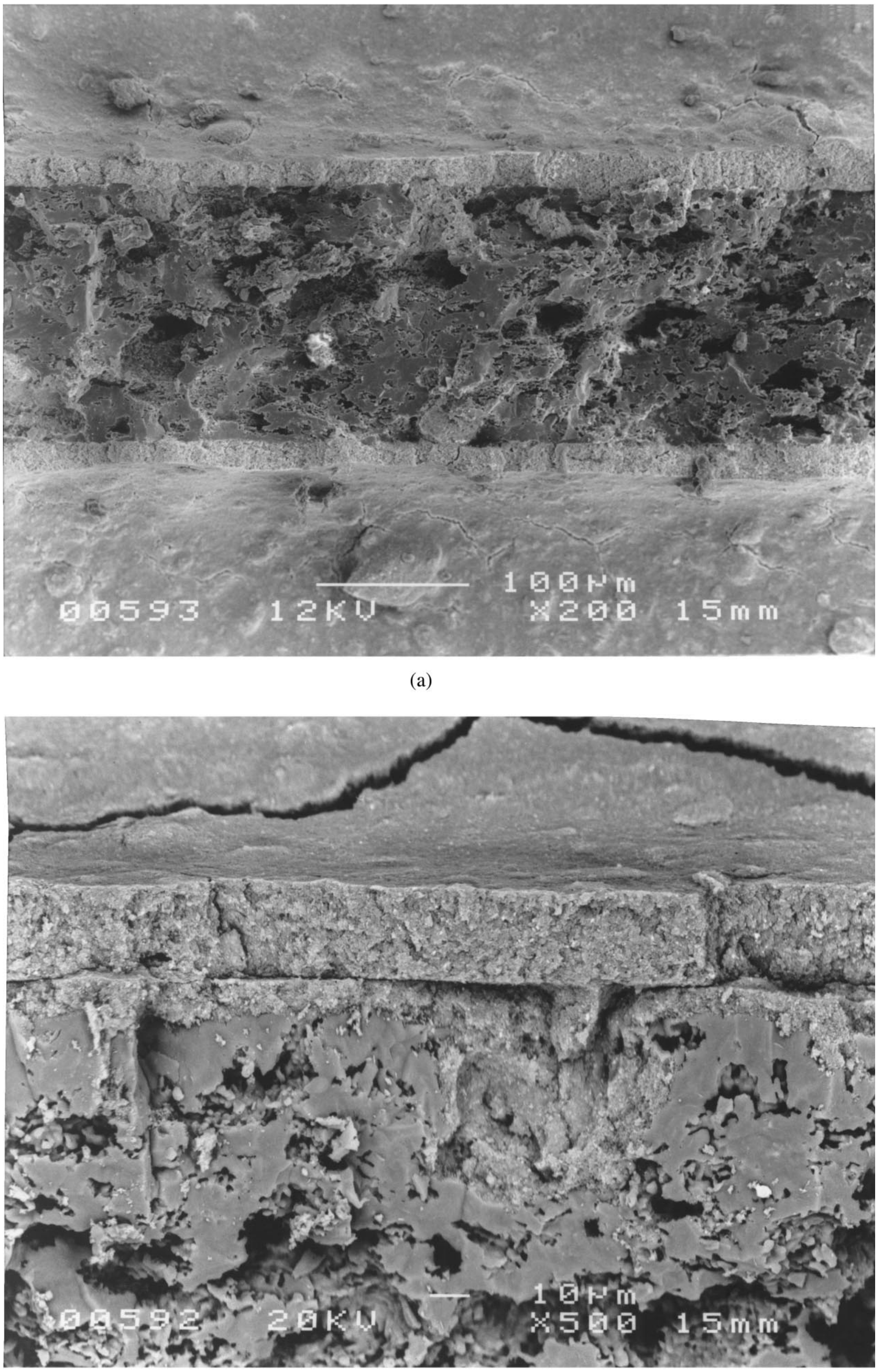
On the curve for the finer particles (Fig. 6b and c) three distinct regions can be observed. In the region of low viscosity—below 50 mPa·s—loading is reproducible, but low, lying between 5 and 7 wt%. A region of intermediate slurry viscosities between 50 and 200 mPa·s follows, where the loadings achieved are in the range 10–20 wt%. Loading in this viscosity region is also characterized from good reproducibility, with the exception of slurry viscosity close to 200 mPa·s. Transition to even higher viscosity values—above 200 mPa·s—shifts the loading to values greater than 25%, inducing though, larger scattering among the values of the loading percentage achieved.

For the coarser particles and for the range of solids content employed, loading seems to vary proportionally with the slurry viscosity and there is no clear transition from one viscosity region to another. Extension of experiments with the coarser particles to higher solids contents would probably reveal the same trend, i.e. a transition to high viscosity—high loading region and loading achieving a plateau value. For the coarser particles the upper viscosity limit for reproducible loading seems to be around 150 mPa·s. Again, loading achieved under these conditions varies between 10–15 wt% and is characterized from good reproducibility.

For slurries of a specific solids content, the use of NH$_4$-PMA instead of HCl, results in lower viscosity values (especially with the coarser particles) as well as better loading reproducibility. With the use of NH$_4$-PMA, slurries of finer particles up to 40 wt% solids content can be handled, resulting in a loading percentage of the order of 15% with good reproducibility. A typical SEM picture of a honeycomb channel (top view) covered with a powder of $d_{90} = 2$ μm under these conditions, is shown in Fig. 7a. The washcoat layer of uniform thickness can be distinguished on both sides of the substrate wall. Larger magnification (Fig. 7b) shows that the thickness of the washcoat layer is of the order of 25 microns.

3.6. Effect of the number of impregnations on loading percentage

The required loading of a honeycomb with the washcoat layer depends on the particular application, and can be as high as 20–30 wt%. This loading cannot always be achieved with a single impregnation; successive impregnations are often required until the total amount of washcoat is deposited upon the honeycomb. Loading percentage as a function of the number of impregnations and solids content is presented in Fig. 8a–d for the two particle size distributions used and for the two deflocculants, HCl and NH$_4$-PMA. For the most dilute slurries of 30% solids content, loading percentage ranges between 5–7 wt% for each impregnation, irrespective of the powder particle size and the deflocculant used. A total loading slightly less than 20 wt% can be achieved with three impregnations. As the slurry becomes thicker (solids content 35%) the loading percentage per impregnation increases and ranges between 5–10%. A total loading between 20 and 25% is achieved with three impregnations. At 40% solids content the viscosity difference between coarser and finer particles becomes significant and affects the number of impregnations required for a specific loading: the more viscous slurry exhibits the highest total loading (31% achieved with



(a)

(b)

Figure 7 Coated monolith: (a) Top view of coated channel, (b) magnification of the coating layer/substrate wall interface.

two impregnations), and the least viscous the lowest (22% achieved with three impregnations). With slurries of 45% solids content one impregnation is enough for the achievement of loading between 15–25 wt%, depending on the slurry viscosity, but as it has been already mentioned, loading under these conditions suffers from poor reproducibility from sample to sample.

4. Discussion

The natural pH of γ-alumina slurries lied in the range 9.0–9.2. At this pH though, the slurries were unstable and settled fast, a fact that was further verified by the respective value of zeta-potential (–20 mV, Fig. 2a). Therefore, improvement of the slurry stability was required. When only either HCl or NaOH were used for pH adjustment, the isoelectric point of alumina occurred around 7.7, a value in agreement with previous studies [13]. The highest value of zeta-potential (+41 mV) was observed at pH around 4.5. On the other end of the pH spectrum, addition of NaOH until a pH of 10.0 was exceeded, was required for satisfactory dispersion.

Addition of deflocculant has shifted in one hand the slurry pH to slightly higher values (from 9.0–9.2 to around 9.5), and on the other hand the whole zeta

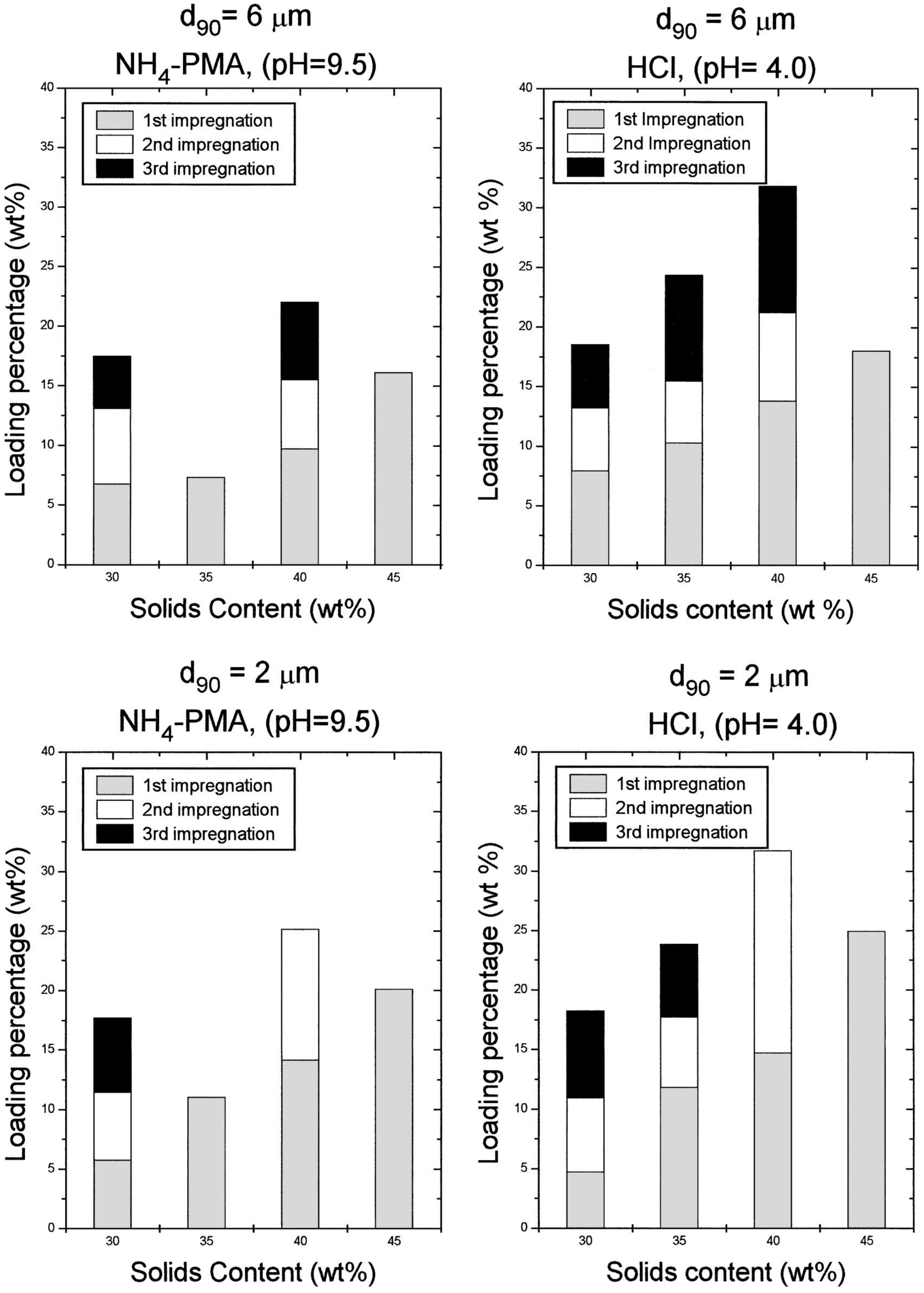


Figure 8 Loading percentage achieved from the various slurries as a function of the number of impregnations.

potential-pH curve towards lower pH values and the isoelectric point from 7.7 to 5.5 (Fig. 2a). The combined result, as observed also by DeLiso *et al.* [14], is that, without any other pH adjustment, the deflocculant alone brings the suspension to the condition of optimum dispersion. The minimum deflocculant concentration required for that is about 1 wt %.

This behaviour is typical for the particular deflocculant and has been also observed for a-alumina [9, 14] and zirconia slurries [14]. At pH values lower than the isoelectric point, the powder surface is positively charged, whereas the opposite happens for pH values higher than 7.7. Cesarano *et al.* [8, 9] have shown that at pH values greater than 8.5 the polyelectrolyte dissociates almost completely and produces highly negatively charged anions that exhibit high affinity absorption on the a-alumina powder. Due to this increase in the negative charge, the isoelectric point of the powder shifts towards lower pH values. This has as a consequence the existence of a larger pH region where the zeta-potential is high and the slurry much better dispersed. On the contrary, the negligible polyelectrolyte dissociation at pH lower than 4.0 makes it a much less effective deflocculant at acidic pHs.

In summary, in addition to dispersion with HCl until $\text{pH} = 4.5$, equally good dispersion of the alumina slurry can be achieved with the addition of 1 wt % NH_4-PMA. This addition does not alter significantly the "natural" pH of the slurry, bringing it to a value around 9.5. The conditions with the use of NH_4-PMA are much milder and the strongly acidic environment required for the case of HCl, which can cause corrosion problems, can be avoided.

The slurry viscosity depends on solids content, powder particle size and deflocculant addition. The combination of high solids content and fine particles can lead to slurries with very high viscosity (Fig. 4). The drastic increase of slurry viscosity as the percentage of the colloidal particles in the slurry is increased, is observed because for the same solids content, the distance between particles becomes shorter as the size of the particles becomes smaller. Consequently the attractive forces are larger and the fluidity less. Extremely high viscosity values for slurries of colloidal particles have been frequently observed in the literature [15, 16]. Smith and Haber [16] studied the effect of solids content and deflocculant concentration on slurry viscosity for slurries of a-alumina powders with similar characteristics as in this study (batches of $d_{50} = 0.6$ and $d_{50} = 6.0\ \mu\text{m}$). They found that viscosity values for the same solids content (78 wt %) and deflocculant concentration were at least an order of magnitude higher in the case of finer particles.

Addition of deflocculant has a beneficial effect in reducing the slurry viscosity: for a specific solids content and powder particle size, slurries with NH_4-PMA are less viscous than the respective slurries with HCl. However, the extent of this viscosity reduction depends also on the powder particle size: with finer particles, the difference between the viscosities of slurries stabilized with HCl and NH_4-PMA is much smaller. This is due to the large percentage of colloidal particles which renders the slurries much thicker so that the dispersing properties of NH_4-PMA cannot improve dramatically the slurry viscosity. In contrast, the beneficial effect of NH_4-PMA on viscosity as the solids content in the slurry is increased, is much more prominent in the case of coarser particles (Fig. 4).

For both particle size distributions the dependence of loading percentage on slurry solids content follows the respective viscosity trend. Loading is low at low solids content and increases progressively as the solids content in the slurry and therefore the viscosity is increased. At low solids content the minor viscosity differences between slurries with different deflocculants, result in minor differences upon the loading achieved as well. As the solids content is increased, slurries become thicker and the viscosity difference among the various slurries becomes more prominent, especially for the coarser particles (Fig. 4). For the coarser particles this viscosity difference has a direct effect on the loading percentage: for the same solids content, slurries of higher viscosity (because of a different deflocculant) produce higher loading percentages. The difference in loading achieved is increasing with increasing solids content just like the viscosity difference. The same analogy between viscosity and loading achieved is observed for the fine particles: in this case the difference between the average loading values for the two different deflocculants as the solids content is increased, is not so significant, just like the relevant viscosity difference observed.

From all the above it is evident that slurry properties and especially the viscosity and the powder particle size play a crucial role both on the magnitude and on the reproducibility of the loading percentage achieved. The similar trend observed for both deflocculants (NH_4-PMA and HCl) for each particle size (Fig. 6a and b), indicates that for a particular particle size distribution, there exists a unique dependence of loading from the slurry viscosity, irrespective of which electrolyte has been used for viscosity adjustment. For each particular particle size there exists a slurry viscosity value beyond which loading percentage reaches a plateau average value, becoming at the same time irreproducible and random. The finer the particle size, the lower is this threshold viscosity value.

Between two slurries of fine and coarser particles with the same viscosity, the one with the coarser particles can accommodate a higher solids content and therefore can achieve a higher loading percentage. This is the reason why the loading percentage—viscosity curve corresponding to the coarser particles, lies in all cases above the respective one for the fine powders.

For the coating process to be efficient, loading with the desired amount of washcoat should take place with a minimum amount of impregnations. When the slurry becomes very thick (i.e. $d_{90} = 2\ \mu\text{m}$, HCl), loading is more or less random and successive impregnations can achieve higher loading percentages than the first one. For all the other cases where the slurry viscosity is low, loading percentage achieved with the first impregnation is slightly higher than that achieved with successive impregnations. This happens because during the first impregnation a certain amount of the slurry fills the pores of the substrate, which are exposed to the channels' outer surface. However, as it is clear from Fig. 7b there exists a significant difference in pore size distribution between the substrate and the washcoat layer. Since the washcoat layer is microporous, during subsequent impregnations penetration of the particles of the slurry into it does not take place, but the second layer is deposited only on top of the first. The passage of water after the first washcoat layer has been deposited on the substrate, has been recommended, in order to facilitate the adhesion of the successive layers with the aid of attractive forces. In this study we have tried this approach but we did not observe any improvement in loading percentage.

To summarize, it seems that when the particle size of the solids is of the order of 2 microns, the best results in terms of reproducibility of the washcoat loading, keeping at the same time the number of impregnations minimum, are achieved with slurries of solids content of 35 wt % using HCl and of 40 wt % using NH_4-PMA. For the coarser particles ($d_{90} = 6$ μm) the respective solids content can be somehow higher, i.e. 40 wt % with the use of HCl and 45 wt % with the use of NH_4-PMA. Under these conditions, a total loading exceeding 20% can be achieved with two impregnations.

5. Conclusions

The coating of cordierite honeycomb specimens with γ-alumina slurries was investigated with the aim to correlate the rheological properties of the slurry to the loading efficiency and to the washcoat quality. For the coating process to be efficient, loading should take place with a minimum amount of impregnations. In order to minimize the number of impregnations and simultaneously deposit an adequate amount of washcoat on the support, the solids content of the slurry has to be high. This requirement can lead to high viscosity values. High viscosity, besides making the slurry more difficult to handle, can result in non-uniform loading or plugging of the honeycomb channels. Loading percentage is only one of the factors that should be taken into consideration. Of equal importance is the quality of the washcoat layer in terms of homogeneity and reproducibility.

Therefore, adjustment of the slurry viscosity is required and this can be achieved with the use of either inorganic electrolytes or organic deflocculants. For optimum loading conditions, the slurry viscosity has to be adjusted between 50–150 mPa·s. Slurries with viscosity in this range, can be obtained, with a solids content of up to 45 wt %, depending on the particle size and the deflocculant used. Under these conditions a total loading exceeding 20% can be achieved with two impregnations. The use of NH_4-PMA compared to that of HCl, provides for lower slurry viscosity for the same solids content, better reproducibility of the loading percentage and in addition can take place in a pH region slightly above neutral avoiding thus the highly acidic environment when HCl is used.

References

1. V. BLACHOU, D. GOULA and C. PHILIPPOPOULOS, *Ind. Eng. Chem. Res.* **31** (1992) 364.
2. T. SHIMROCK, R. D. TAYLOR and J. COLLINS, Eur. Patent 0157651 (1985).
3. Z. R. ISMAGILOV, G. V. CHERNYCH and R. A. SKRABINA, in "Catalysis and Automotive Pollution Control III—Studies in Surface Science and Catalysis Vol 96," edited by A. Frennet and J. M. Bastin (Elsevier Science, Amsterdam, 1995) p. 387.
4. A. F. M. LEENAARS and A. J. BURGRAAF, *J. Coll. and Int. Sci.* **105**(1) (1985) 27.
5. L. L. MURRELL and S. J. TAUSTER, in "Catalysis and Automotive Pollution Control II," edited by A. Crucq (Elsevier Science Publishers B. V., Amsterdam, 1991) p. 547.
6. G. K. NARULA, W. L. H. WATKINS and M. SHELEF, US Patent no. 5210062 (1993).
7. E. DELISO, W. VAN RIJSWIJK and W. R. CANNON, *Coll. and Surf.* **53** (1991) 383.
8. J. CESARANO, I. A. AKSAY and A. BLEIER, *J. Amer. Ceram. Soc.* **71**(4) (1988) 250.
9. J. CESARANO and I. A. AKSAY, *ibid.* **71**(12) (1988) 1062.
10. S. BAKLOUTI, C. PAGNOUX, T. CHARTIER and J. F. BAUMARD, *J. Eur. Cer. Soc.* **17** (1997) 1387.
11. A. B. CORRADI, T. MANFREDINI, G. PELLACANI and P. POZZI, *J. Amer. Cer. Soc.* **77**(2) (1994) 509.
12. G. TARI, J. M. F. FERREIRA, A. T. FONSECA and O. LYCKFELDT, *J. Eur. Ceram. Soc.* **18** (1988) 249.
13. I. I. M. TIJBURG, J. W. GEUS and H. W. ZANDBERGEN, *J. Mater. Sci.* **26** (1991) 6479.
14. E. DELISO, W. R. CANNON and A. S. RAO, in "Advances in Ceramics, Vol. 24: Science and Technology of Zirconia III" (The American Ceramic Society, 1988) p. 335.
15. Z. ZHANG, L. HU and M. FANG, *Amer. Cer. Soc. Bull.* **75**(12) (1996) 71.
16. P. A. SMITH and R. A. HABER, *Ceram. Eng. Sci. Proc.* **10**(1–2) (1989) 1.

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