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The deposition of γ-Al_2O_3 layers on ceramic and metallic supports for the preparation of structured catalysts

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Abstract

Deposition of γ-Al_2O_3 washcoats onto Aluminium and FeCrAlloy® supports in the form of slabs and onto α-Al_2O_3 tubes was performed according to a two-step procedure involving: (a) deposition of a bohemite primer, (b) deposition of the γ-Al_2O_3 layer, both by dip coating into powder dispersions in HNO_3 aqueous solutions. We present herein data concerning the effects of the major preparation variables (HNO_3 and H_2O concentrations in the dispersion, withdrawal velocity, drying temperature, number of dipping cycles, calcination temperature) on the deposited coating load and on the adherence of the washcoat. Based on a rheological characterisation of the γ-Al_2O_3 dispersions, we propose also a correlation between their apparent viscosity and the washcoat load. Finally, we briefly illustrate the activity in catalytic combustion reactions of structured Pd-based catalysts prepared according to the investigated washcoating methods. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Al_2O_3; Washcoat; Ceramic and metallic supports

1. Introduction

Monolithic catalysts have become the most diffuse and economically significant application of catalytic reaction engineering and industrial catalysis so far. This is due to the commercial success of such well-known environmental catalysis processes as the purification of exhaust gases from automobiles, the abatement of NO_x emitted in the stack gases from power stations by the selective catalytic reduction process, and the catalytic combustion of VOCs. Several hundred millions of monolithic catalytic converters are currently in operation on cars and vehicles throughout the world; over 150,000 m^3 of SCR-DeNO$_x$ honeycomb catalysts have been delivered and installed, mostly in Japan and in Europe. As a consequence, competencies associated with monolithic catalysts are now more and more relevant also to practitioners and applied researchers in areas outside traditional chemical engineering and catalysis, including, e.g. the fields of energy production, car manufacturing and pollution control. In view of the dramatic importance of energy and environmental issues, we can expect this trend to continue and even grow in the future.

Although monolithic and structured catalysts are so commonly used, however, very little is available so far in the open and scientific literature about their preparation methods. This work presents a fundamental study on a method for preparing catalytic structured catalysts by washcoating of inert supports. We discuss herein a procedure for the dip coating of both metallic and ceramic supports with a simple γ-Al_2O_3-based system, starting from a commercial γ-Al_2O_3 submicronic powder, and we illustrate the influence of the main

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related preparative variables on such characteristics of practical importance as the specific load of deposited washcoat and its adherence, the goal being to obtain guidelines for the rational selection of the preparation method with respect to the desired features of the catalytic layers.

Finally, we illustrate briefly the catalytic activity of two different kinds of structured catalysts with Pd as active element, prepared according to the discussed methods and tested in an annular and in a plate-type reactor in the oxidation of CH_4 and CO, respectively.

2. Experimental

2.1. Preparation of the coated samples

The proposed washcoating method consists of: (i) support pre-treatment, (ii) primer deposition and (iii) coating deposition.

2.2. Support pre-treatment

Either slabs of commercial Aluminium and FeCrAlloy® or tubes of dense α-Al_2O_3 were used in this study as representative of metallic of ceramic structured supports. Only the metallic supports were pre-treated before washcoating, as reported in the following.

Aluminium slabs were immersed in HCl solutions at RT for 2–3 min to improve superficial roughness and subsequently in HNO_3 solutions at 80°C for 5 min to favour the formation of superficial oxides. It is well known from the literature [1] that this kind of treatment results in the formation of an alumina oxide layer which improves greatly the adherence of the deposited γ-Al_2O_3 layers. XRD patterns did not show the peaks of aluminium oxides, probably because the relative amount of such oxides is very small, but SEM images confirmed that small particles of aluminium oxide were formed on the surface after the treatment with acid.

FeCrAlloy® slabs were calcined at 900°C for 10 h. This thermal treatment caused the segregation of an alumina layer on the metallic surface. This phenomenon is well documented in the literature [1,2]. XRD patterns showed clearly the peaks associated with α-Al_2O_3 and SEM analysis evidenced the formation of the characteristic ‘alumina whiskers’.

Before starting the coating procedure all the supports were washed with acetone to remove the superficial impurities due to manipulation.

2.3. Primer deposition

The use of a primer to improve the adherence of the washcoat layer is well known in the literature [1,3]. In our case, since we wanted alumina to be the only material deposited onto the supports, we adopted a bohemite primer prepared by dispersing 10% (w/w) of a commercial aluminium hydroxide powder (Disperal®, Condea Chemie) in a 0.4% (w/w) HNO_3 aqueous solution. After mixing for 10 min, a stable dispersion of bohemite was obtained. According to the supplier’s specifications, the viscosity of such a dispersion increases from 2 to 20 mPa s in 2 days: this was confirmed by our own rheologic measurements. We also studied the pH variation with time of the Disperal dispersion: the pH value grew from 1.3 to 3.5 in about 70 h, then the solution slowly approached the final pH of about 4 (10 or more days later). Based on such results, the dispersion was prepared at least 2 days before its use as a primer. On the other hand, it was found stable and suitable for our applications until 6 months after the preparation.

For the primer deposition, the supports were dipped in the bohemite dispersion, withdrawn at a controlled speed of 3 cm/min, and dried at room temperature for 30 min. This resulted in the formation of a well adherent layer on the surface of all the supports. SEM images showed that such layers were uniform, with an estimated thickness of 1–2 μm.

2.4. Coating deposition

A commercial γ-Al_2O_3 submicronic powder (Sumitomo ALKPG-0015) was dispersed in a HNO_3 aqueous solution with the following typical proportions:

$$HNO_3/Al_2O_3 = 2.16\,\mathrm{mmol/g},$$
$$H_2O/Al_2O_3 = 3.2\,\mathrm{g/g}$$

After vigorous stirring for about 16 h in a closed reactor at a constant temperature of 18°C, the dispersions were suitable for deposition. At this stage the supports, already pre-coated with the bohemite primer, were dipped in the alumina dispersion for 15 s and then withdrawn at a constant speed of 3 cm/min. The withdrawal velocity was accurately controlled because it is well known from the dip coating theory [4,5] that the coating thickness varies with this parameter.

The coated samples were eventually 'flash' dried at 280°C for 5 min in a ventilated oven. To study the influence of the H_2O and HNO_3 slurry contents, a number of slurries were prepared with varying HNO_3/Al_2O_3 ratios at constant H_2O/Al_2O_3, and with varying H_2O/Al_2O_3 ratios at constant HNO_3/Al_2O_3. It is worth mentioning that the same procedure was successfully applied also to the deposition of γ-Al_2O_3 coatings onto Cu slabs: discussion of the related data is, however, beyond the scope of the present paper.

2.5. Characterisation of the coated samples

The prepared samples were characterised by gravimetric analyses, SEM images (Electron Scanning Microscope DSM 940 from Zeiss), BET analyses (Sorptomatic 1900 Fision BET instrument, using the N_2 absorption technique), and ultrasound adherence tests. The rheological characteristics of each starting slurry as a function of the shear rate (flow curves) were determined using a rotational rheometer (Dynamic stress rheometer DSR 200 by Rheometrics). The influence of the main preparation variables is discussed in the following.

3. Results and discussion

3.1. Coating load

3.1.1. Effects of HNO_3 and H_2O concentration in the starting dispersion

We have investigated a range of HNO_3/Al_2O_3 ratios in the slurry between 0.36 and 8.65 mmol/g at constant $H_2O/Al_2O_3 = 3.2\,g/g$.

The resulting slurries were used to coat both aluminium slabs and α-Al_2O_3 tubes. The load of deposited coating was determined by weighing, while the coating thickness was measured by SEM. As shown in Fig. 1, the plot of the deposited coating load per unit surface area versus the HNO_3 concentration in the slurry goes through a maximum at 4.33 mmol/g HNO_3/Al_2O_3. The deposited layers with an acid/alumina ratio greater than or equal to 3.6 mmol/g were poorly adherent. A similar trend was observed for a variety of supports.

The results of the rheologic measurements are helpful in interpreting the data in Fig. 1. From the flow curves we observe that for HNO_3/Al_2O_3 ratios less than or equal to 2.16 mmol/g, the slurries exhibited a pseudo-Newtonian behaviour, the viscosity remaining constant with increasing shear rate. For greater HNO_3/Al_2O_3 ratios the slurries became markedly non-Newtonian, their viscosities decreasing with increasing shear rate (shear-thinning behaviour). Remarkably, if viscosity values are plotted versus the

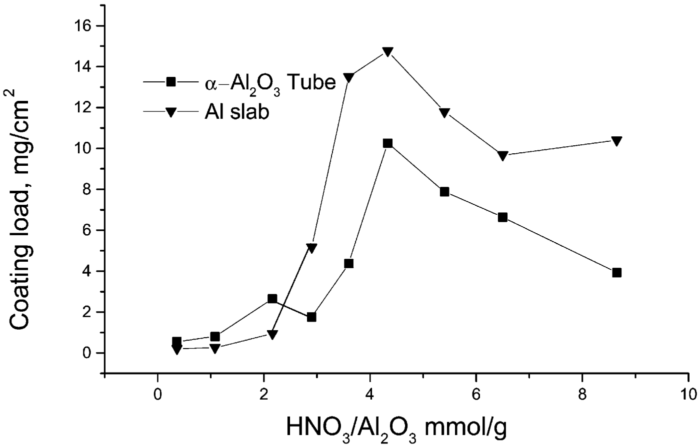

Fig. 1. Deposited coating load versus slurry HNO_3 concentration, $HNO_3/H_2O = 3.2\,g/g$.

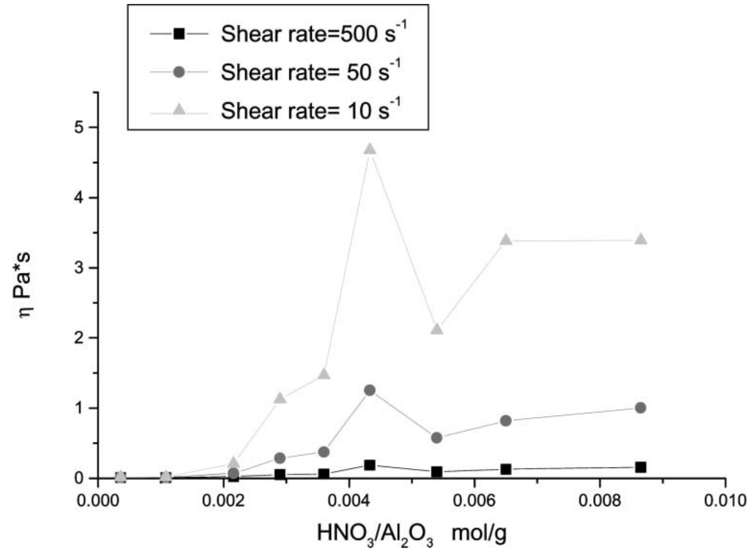

Fig. 2. Slurry viscosities versus HNO_3 concentration at different shear rates.

HNO_3/Al_2O_3 ratio at a constant shear rate (Fig. 2), we obtain the same trend exhibited by the coating load (Fig. 1), again with a maximum at $HNO_3/Al_2O_3 = 4.33$ mmol/g. This correlation points out the key role of the slurry flow behaviour in determining the thickness of the coating layer. On the other hand, the slurry viscosity is likely controlled by a gelation process, as described in [4]. The complex influence of the acid concentration on the gelation process is currently under investigation.

Based on the above results, in the following other effects were investigate using samples prepared from slurries with HNO_3/Al_2O_3 ratios less than 2.9 mmol/g.

To investigate the effect of the H_2O content, slurries prepared with H_2O/Al_2O_3 ratios varying from 2.8 to 3.6 g/g at constant $HNO_3/Al_2O_3 = 2.16$ mmol/g were used to coat aluminium slabs as well as α-Al_2O_3 tube pieces. The results pointed out that the H_2O content in the slurry is a key parameter of the process. The coating load per unit surface area decreased monotonically with increasing H_2O/Al_2O_3 ratio, and approached an asymptote for ratios greater than 3.3 g/g (Fig. 3). The coating layers were well adherent in all cases except for the smallest H_2O/Al_2O_3 ratio = 2.8 g/g. Probably in this case there is a lack of dispersing medium for the alumina particles, so that the resulting slurry is not adequate for the deposition process.

3.1.2. *Effect of withdrawal velocity*

The effect of the withdrawal velocity in the dip coating process was studied between 1.7 and 7.6 cm/min: in such a range the coating load increased only slightly with increasing velocity. Selected results are shown in Fig. 4. Notably, existing theories for free coating with

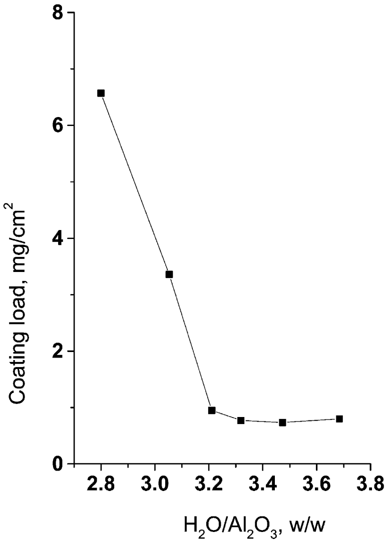

Fig. 3. Deposited coating load versus slurry H_2O content, $HNO_3/Al_2O_3 = 2.16$ mmol/g.

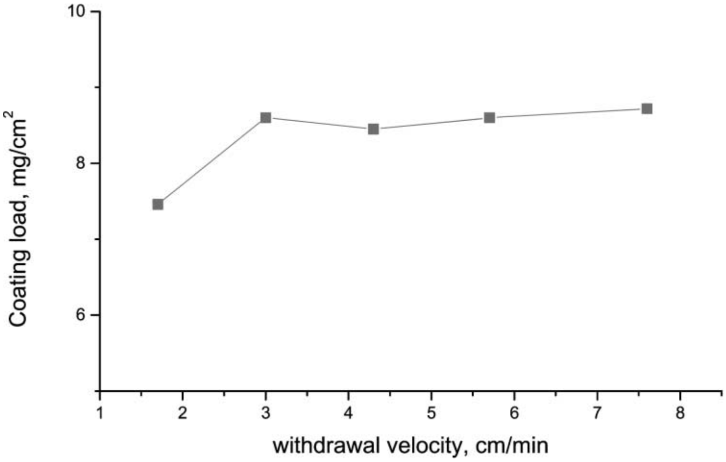

Fig. 4. Effect of withdrawal velocity on the coating load, $HNO_3/Al_2O_3 = 2.9$ mmol/g.

Newtonian fluids [4,5] predict a stronger dependence than apparent in Fig. 4.

3.1.3. Multiple depositions

Deposition of multiple layers onto the same slab was also attempted, starting from a slurry with a $HNO_3/Al_2O_3 = 2.16$ mmol/g and $H_2O/Al_2O_3 = 3.2$ g/g. For each layer, we repeated exactly the same procedure used for the single layer sample. We observed that it is possible to deposit two catalyst layers, reaching a coating load of about 2.3 mg/cm^2, still maintaining a good adherence. Deposition of a third layer, however, caused the loss of adherence of all the materials coated onto the support.

3.1.4. Coating density

Fig. 5 illustrates the linear correlation between the coating loads deposited onto various samples and the corresponding coating thickness, as determined from SEM images. Accordingly, the deposited layers have the same density value of about 0.9 g/cm^3, estimated from the slope of the regression line.

3.2. Coating adherence

The adherence of the flash dried coatings has been evaluated according to a method described in the patent literature [1], based on the measurement of the weight loss caused by exposure to ultrasounds. The coated slabs were immersed in petroleum ether inside a sealed beaker, and then treated in an ultrasound bath for 30 min.

The effect of the slurry composition, and specifically the HNO_3/Al_2O_3 ratio has been first investigated. As shown in Fig. 6, the samples obtained from slurries with HNO_3/Al_2O_3 ratio ≤ 2.2 mmol/g showed no weight loss, whereas samples associated with HNO_3/Al_2O_3 ratios of 2.9 mmol/g gave $\approx$11% weight loss; samples with higher ratios gave weight losses in excess of 25%. Accordingly, optimal adherence is achieved for HNO_3/Al_2O_3 ratios less than 2.9 mmol/g. The reasons for this behaviour have not been completely clarified yet. Indeed a correlation between the coating load (and thickness), which increases with the HNO_3/Al_2O_3 ratio, and the decline of the coating adherence is evident which suggests an influence of thermo-mechanical stresses generated by the drying process. However, a role of “chemical” effects associated with the gelation process of the slurry cannot be ruled out.

The effect of the post-deposition procedures, i.e. drying and calcination, has been then investigated. No significant influence of the drying temperature on the coating adherence was detected, provided that drying was performed at temperatures greater than 100°C. To investigate the influence of the calcination temperature on the adherence of the coating layers FeCrAlloy® slabs were used instead of Al slabs to allow calcination of the coated samples up to high temperatures. FeCrAlloy® slabs were coated

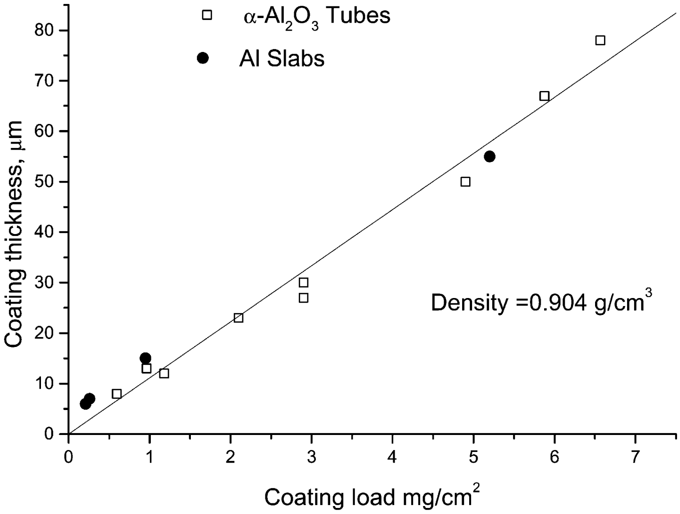

Fig. 5. Density of the slurries.

as described above using a slurry with HNO_3/Al_2O_3 ratio of 2.9 mmol/g. For the uncalcined sample, the weight loss during the standard adhesion test in the ultrasound bath was 11.3%. Calcination temperatures of 400, 700 and 900°C for 10 h resulted in weight losses of 1.6, 0.8 and 0.08%, respectively. Similar improvements were obtained also with samples corresponding to other HNO_3/Al_2O_3 ratios. This suggests that increasing the calcination temperature generally enhances the adherence of the washcoat layer.

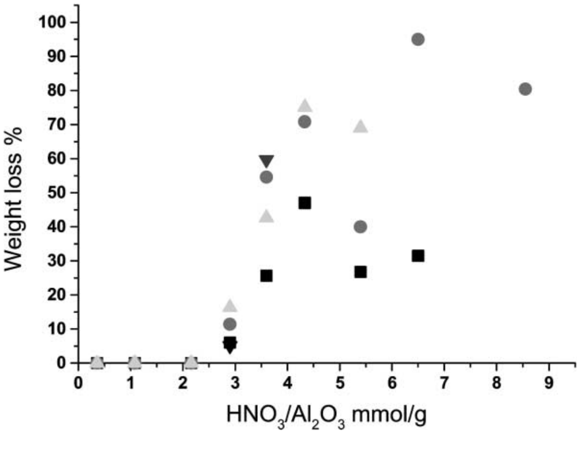

Fig. 6. Effect of the HNO_3 slurry content on the coating adherence in ultrasound bath tests. Symbols represent results of replicated runs.

3.3. Catalytic activity

γ-Al_2O_3 coated structured catalysts prepared with Pd as the active element were tested in a plate-type and in an annular reactor, using oxidation of CO and CH_4 as model reactions, respectively. To prepare a catalytically active layer for these purposes, γ-Al_2O_3 powder (Sumitomo) was impregnated via incipient wetness with a $Pd(NO_3)_2$ solution, to obtain a composition of 3% (w/w) Pd in the case of CO combustion and 10% (w/w) Pd in the case of CH_4 oxidation. The impregnated powders were dried overnight at 110°C in a ventilated oven and then dispersed in a HNO_3 aqueous solution and deposited according to the same procedure described in Section 2. The addition of Pd somehow affected the properties of the resulting washcoats, which were found thicker than the corresponding coatings of pure γ-Al_2O_3 prepared with the same composition ($HNO_3/Al_2O_3 = 2.16$ mmol/g, $H_2O/Al_2O_3 = 3.2$ g/g). This aspect will be addressed in future work.

The structured catalysts prepared for the activity tests had a surface area of about 120 m^2/g and a pore volume of about 0.5 cm^3/g. XRD patterns showed only reflections of two crystallographic phases, associated with γ-Al_2O_3 and PdO. After the calcination cycles at 500 and 700°C the morphological properties were not modified. Also catalysts in the form of powders were obtained by dry impregnation of the commercial γ-Al_2O_3 and tested in the same model reactions using a packed bed microflow reactor consisting of a quartz tube ($d_{int} = 6\,mm$) inside a cylindrical oven. Other details on catalyst preparation and characterisation are given in [6].

CO oxidation was carried out on catalysts supported on aluminium slabs (46 mm × 200 mm × 1 mm) assembled in the form of a plate-type reactor [6–8]. The assembled packet of coated slabs was loaded into a stainless steel reactor tube placed inside a furnace. The temperature along the catalytic bed was monitored by five sliding thermocouples. The reaction conditions were: $T_{oven} = 105$–$450°C$, CO feed content $= 0.7$–$9\%\,(v/v)$ in air, GHSV $= 2500$–$150{,}000\,N\,cm^3/(g_{cat}\,h)$. The structured catalysts with aluminium slabs showed a very good activity in the combustion of CO, comparable with the activity of catalyst powders with the same Pd load. However, isothermal conditions were approached even for high concentrations of CO in the feed ($Y^0_{CO} = 0.09$), due to the excellent thermal conductivity of the Al slabs. CO oxidation runs in the microreactor loaded with the same catalyst in the form of powder was limited to a maximum $Y^0_{CO} = 0.035$ due to strong temperature gradients. These results point out that structured metallic reactors have good potential for kinetic studies of strongly exothermic reactions [7,8]. Based on replicated runs, the activity was not significantly modified after a number of experiments covering a period of a few months. Since each experiment involved thermal cycling between RT and the run temperature (up to 450°C), this can be taken as an indication that the deposited catalytic washcoats did not suffer from repeated temperature excursions. Nevertheless, thermal shocks associated with practical applications may be much more severe: accordingly, this aspect will be further pursued in future work.

CH_4 combustion tests were performed in an annular reactor using catalysts supported on dense α-Al_2O_3 tubes ($d_{ext} = 6.5\,mm$). A γ-Al_2O_3 washcoat of 10 μm thickness, containing 10% Pd, was deposited. The coated tube was loaded co-axially in a quartz tube ($d_{int} = 7\,mm$) inside a cylindrical oven. The reaction conditions were: $T_{oven} = 150$–$600°C$, $CH_4 = 0.75\%$ in air, GHSV $= 3{,}000{,}000\,N\,cm^3/(g_{cat}\,h)$. The tube was placed in the quartz chamber in order to obtain an annulus size of 0.2–0.3 mm. Preliminary calculations confirm that such a thin layer and small annulus dimensions grant negligible diffusional limitations up to very high reaction rates (first order rate constant up to $K_c = 10{,}000\,h^{-1}$). Estimates of the reaction rate constants properly accounting for the inhibiting effect of water [7] show that the activity of the catalytic coating in the annular reactor compares well with the combustion activity of the catalyst powders. In the case of the annular reactor extremely high GHSV could be achieved with negligible pressure drop: consequently, much wider temperature ranges (up to 600°C) could be explored under kinetic conditions than in the case of laboratory packed-bed microreactors. Besides a better control of the catalyst temperature is intrinsically associated with the annular reactor, which appears therefore as an excellent candidate for kinetic studies of catalytic combustion reactions [8].

4. Conclusions

Well adherent washcoats, suitable for catalytic applications, were obtained by the deposition of γ-Al_2O_3 layers onto Al and FeCrAlloy® supports in the form of slabs as well as onto α-Al_2O_3 tubes according to a two-step dip coating procedure, which involves also the deposition of a bohemite primer, starting form a commercial submicronic γ-Al_2O_3 powder.

We have investigated the effects of the major preparation variables (HNO_3 and H_2O concentrations in the starting γ-Al_2O_3 aqueous dispersion, withdrawal velocity in the dip coating process, number of dipping cycles, drying temperature, calcination temperature) on the deposited coating load and on the adherence of the washcoat.

Concerning the coating load, the most critical variable turns out to be the HNO_3/Al_2O_3 ratio in the starting aqueous dispersion, while the H_2O content seems to have only a threshold effect. In fact, a rheological characterisation of the γ-Al_2O_3 dispersions has evidenced that their apparent viscosity is also strongly influenced by the HNO_3 concentration, which points to a controlling role of the gelation process in the dispersions.

The coating load can be incremented also by a double dipping procedure. Optimal results are associated with compositions of the dispersion with $HNO_3/\gamma\text{-}Al_2O_3 \approx 2\,\text{mmol/g}$ and $H_2O/\gamma\text{-}Al_2O_3 > 3\,\text{w/w}$, resulting in coating thicknesses around 30 μm.

Concerning the adherence of the coating layer, our data suggest that it can be markedly improved by calcination at high temperatures, whereas it is essentially unaffected by drying temperatures above 100°C.

Finally, the adequacy of the $\gamma\text{-}Al_2O_3$ coatings for catalytic activity has been demonstrated in catalytic combustion reactions over structured Pd-based catalysts prepared according to the investigated washcoating methods.

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