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Low Surface Area Cerium Oxide Thin Film Deposition on Ceramic Honeycomb Monoliths

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In this work, the development of acid-free stable oxide dispersions has been studied to obtain thin oxide layers onto substrates of complex geometry to obtain structured catalysts and reactors for process intensification. In particular, attention has been paid to syngas production in steam reforming process using CeO_2-based oxides. For this purposes commercial cerium oxide (3 m^2 g^{-1}) was selected as model of low surface area catalyst precursor and dip-coating as deposition technique. Ceramic monoliths were used as structured supports (diameter 1 cm, length 1.5 cm). A slurry formulation, including the powder, glycerol, polyvinyl alcohol and distilled water allowed to obtain the proper rheological behavior and stability of the suspension. The addition of a relatively small PVA quantity changes dispersion properties, allowing to properly tune viscosity. Results were evaluated in terms of coating load and adhesion performance. Final coating loads of about 18 %wt. were obtained performing multiple depositions. A good homogeneity of the washcoat layers was found, accompanied by a quite good adhesion (6% wt of coating loss after ultrasound treatment).

1. Introduction

Deposition of thin ceramic layers on geometrical substrates is a very interesting research topic, in in view of many fields of application (Montebelli et al., 2014). Among them, process intensification has recently reached wide attention by both the technological and scientific community. In particular, monoliths and open cell foams have been proposed for syngas production in steam reforming process. In this respect, CeO_2-based oxides have been intensively studied for their oxygen storage capacity (OSC), redox properties and catalytic performances. Due to such properties, this material has been widely used as active phase support in many reforming processes for hydrogen production (Pino et al., 2003).
Many methods are available to deposit catalytic powders on complex geometrical substrates. Usually a two-phase process is performed. It implies first a pretreatment of the geometrical support in order to promote surface interactions between the substrates and the washcoat (Wu et al., 2001) and then the deposition of the washcoat via a proper coating technique. The washcoat can be either a bare morphological support or the final catalyst already. Among the different deposition methods, dip-coating from a sol or a slurry liquid phase is one of the most applied one, being a good compromise between cost, complexity and final product effectiveness (Zhang et al., 2012).
Washcoat properties (i.e. loading, thickness and adhesion) depend both on physic-chemical properties and on rheological behavior of the slurries (Cristiani et al., 2005). Slurries properties, such as stability and rheology, are key features in order to manage layer thickness, load and adhesions. Slurry properties depend on many parameters, such as the nature of the suspended powder, powder particle dimensions, powder loading, nature and concentration of dispersant, temperature and viscosity modulators. In case of high surface area catalysts, a stable solid particle dispersion can be obtained via surface charging with an acidic solution (Valentini et al., 2001) of the powders. Unfortunately, this procedure is confined to chargeable surfaces and/or high surface

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area materials, while it cannot be applied in case of non-chargeable low surface area powders or acid-sensitive surfaces. This is the case of Ce-based materials proposed for steam reforming applications.
Accordingly, in this work the development of an acid-free stable oxide dispersions has been studied to disperse low surface area oxides. Commercial cerium oxide with low surface area (3 m^2 g^{-1}) was selected as model powder and dip-coating was as applied as deposition technique. Slurry rheological behavior was evaluated and viscosity was modulated by using polyvinyl alcohol (PVA), in order to produce a stable dispersion, with proper rheological behavior suitable for deposition. Ceramic monoliths were used as structured supports (diameter 1 cm, length 1.5 cm). Results were evaluated in terms of coating load and adhesion performance was determined by performing an accelerated stress test in ultrasound bath.
The final purpose is to demonstrate that the properties of the obtained slurries can be tuned with the formulation composition and that, in turn, the slurries properties allow to achieve a homogeneous and adherent washcoat layer.

2. Experimental

2.1 Materials

Cordierite monoliths with 400 cell per inch density (CPI) (Applied Ceramics Inc. (USA)) were used as geometrical support for coating deposition.
Low surface area cerium oxide (CeO_2, supplied by Sigma-Aldrich) was used as model powder. It consists of a fluorite structure with a surface area (SA) of 3 m^2 g^{-1} and a pore volume (Vp) of 0.4 cm^3 g^{-1}. According to the procedure reported in literature (Cristiani et al., 2009), surface charging was measured. No surface charging (SC) was detected at any pH value.
For slurry formulation, glycerol (G) (87 % w/w water solution, Sigma-Aldrich) was used as dispersant while polyvinyl alcohol (PVA) (Mowiol, Sigma-Aldrich) with an average molar weight of 67,000 g mol^{-1} was used as plasticizer (Zhang et al., 2012). Distilled water (H) was added as dilutant.

2.2 Procedures

Slurry preparation
The detailed experimental procedure for slurry production has been reported elsewhere (Montebelli et al., 2014).
In a typical preparation, polyvinil alcohol was dissolved in distilled water at 85 °C, under magnetic stirring. Then, glycerol was added in order to obtain the dispersion medium. CeO_2 powder was added to the medium and the mixture was ball-milled for 24 h at 50 rpm constant rotation rate by using ZrO_2 as grinding bodies.
The compositions of the slurries are reported in Table 1. In the Table and all over the text the sample name will be identified by a label which indicates the slurry components: i.e. Ce_HGP_2 identifies a slurry consisting of water (H), glycerol (G) and PVA 2% wt.

*Table 1: Slurry composition resume (*Liquid = water + glycerol)*

Slurry Name	Glycerol/CeO_2 (w/w)	Water/CeO_2 (w/w)	% PVA/liquid* (w/w)
Ce_HGP_0			0
Ce_HGP_2	1.9	1.8	2
Ce_HGP_4			4

The obtained slurry, underwent a pre-treatment in ultrasounds bath for 30 min in order to reduce foaming after the powder dispersion.

Coating deposition
Coating deposition was performed via dipping process. Supports were cleaned by means of ultrasound in acetone bath for 30 min. A self-made dip-coater with adjustable withdrawal velocity was used. Speed was fixed at 13 cm min^{-1} and it was kept constant during the whole withdrawing step. Repeated coating depositions were performed.
Wet samples were flash dried for 6 min at 350 °C in a sealed oven in order to remove the liquid phases. Following, a calcination process was performed at 900 °C for 10 h, using a 2 °C min^{-1} rate for both heating and cooling ramps.

2.3 Characterization

A rotational rheometer was used in order to assess dispersion rheological properties (Stresstech 550, Reologica Instruments). For the analyses, parallel disk geometry plates were used (40 mm diameter, 0.5 mm gap). Test were performed by evaluating viscosities in the shear rates range 10^{-2}-10^{3} s^{-1}.
Washcoat deposition was evaluated by gravimetric analysis, by weighting the bare and the coated support before and after both flash drying and high temperature thermal treatments.
According to a procedure reported elsewhere (Cristiani et al., 2012), washcoat adhesion was evaluated after 30 min of accelerated stress test in petroleum ether ultrasound bath.
Coating layers homogeneity and morphology were evaluated by means of scanning electronic microscope (SEM) (Stereoscan 360, Cambridge Instruments).

3. Results and discussion

The rheological behaviour of dispersions is reported in Figure 1. The addition of a relatively small PVA quantity changes dispersion properties, allowing to properly tune viscosity. The latter is a key parameter during coating deposition, especially when dip coating process is employed. For this reason, a wide range rheology analysis was performed on the slurry.

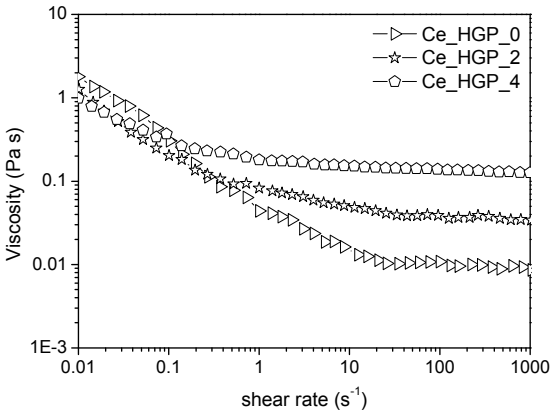

Figure 1: Rheology properties of cerium oxide-based slurries

Flow curves display a light shear-thinning behaviour in the range of interest for dip-coating application. As PVA content increases, the non-Newtonian part of the flow curve moves towards lower shear rate values. Moreover, higher viscosity values are obtained in the Newtonian region at higher shear rates. At 10 s^{-1} of shear rates a viscosity value equal to 0.050 Pa s is measured for sample Ce_HGP_2; the latter is suitable for washcoat deposition on monoliths (Agrafiotis and Tsetsekou, 2000).
Results concerning final washcoat load, thickness and adhesion are reported in Figure 2. Only results related to the sample Ce_HGP_2 are reported. Further investigations need to be accomplished in order to extend washcoating analysis to the other slurries.

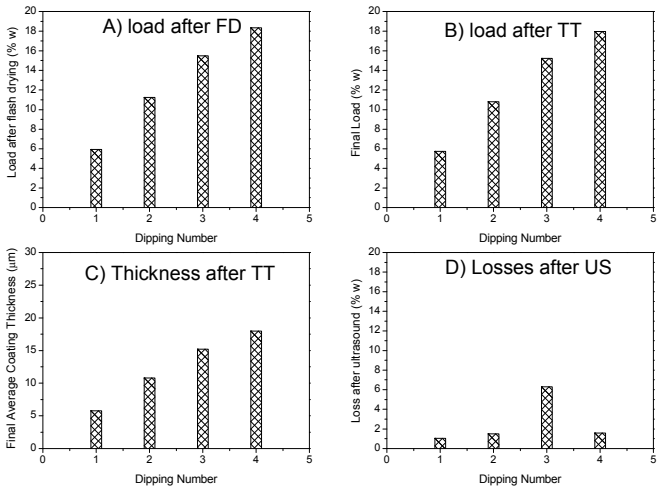

Figure 2: Washcoat deposition evaluation: load after flash drying (A), final load (B), final average coating thickness (B) ad losses after adhesion test (D)

Coating load clearly depends on multiple dipping. This behaviour is already present in Flash Dried samples (FD) and it is preserved upon Thermal Treatment (TT) (Figure 2-A,B). A high reproducibility of the process was found upon repeating the whole process on different monoliths: very close values of coating loads were obtained for different monoliths dipped with the same number of dipping. The load increase is substrate surface-dependant: washcoat amount deposited after each dipping progressively decreases, possibly pointing out a sort of sensitiveness of the coating layer towards the nature of the surface of the layer deposited immediately before. This trend is of course also found by the coating thickness obtained by calculation (Figure 1-C). Coating thickness indeed cannot be directly measured thus it was obtained by applying the Eq(1).

$$Final\ Average\ Coating\ Thickness = \frac{Washcoat\ [g]}{Washcoat\ Density\ [g\ m^{-3}] \cdot Monolith\ Surface\ [m^2]} \quad (1)$$

Coating thickness of about 18 µm have been calculated after 4 dipping process. These values have been report as suitable for the considered catalytic application. Adhesion test results are reported in Figure 2-D. Low coating losses after accelerated stress test due to sonication are shown, that resulting in a pretty good washcoat-substrate interaction.
Surface analysis performed by scanning electronic microscope is reported in Figure 3.

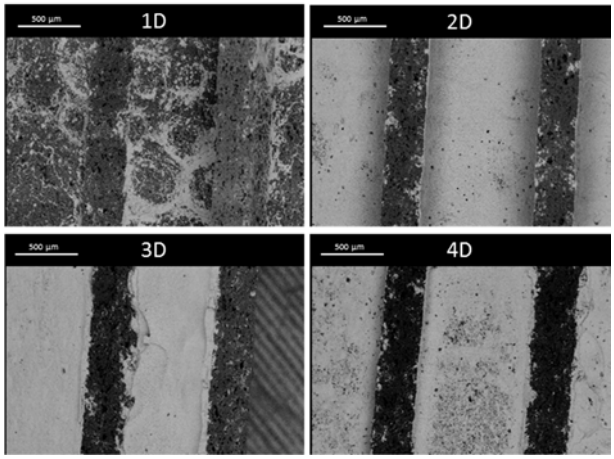

Figure 3: SEM analysis in back-scattering mode of monolith inner channels

Results were obtained in back-scattering acquisition mode, in order to differentiate coating and substrate due to the difference of atomic numbers of the constituents. The lighter areas (grey or light grey in the pictures) refers to cerium oxide layers, while the darker (black or dark grey) refers to the uncovered monolith. A clear trend is noticeable as washcoat uniformity increases with dipping number: after one dipping, monolith surface coating is still not homogeneous, while starting from two dipping on almost complete coverage is reached.
An attempt of thickness evaluation by SEM analysis is reported (Figure 4).

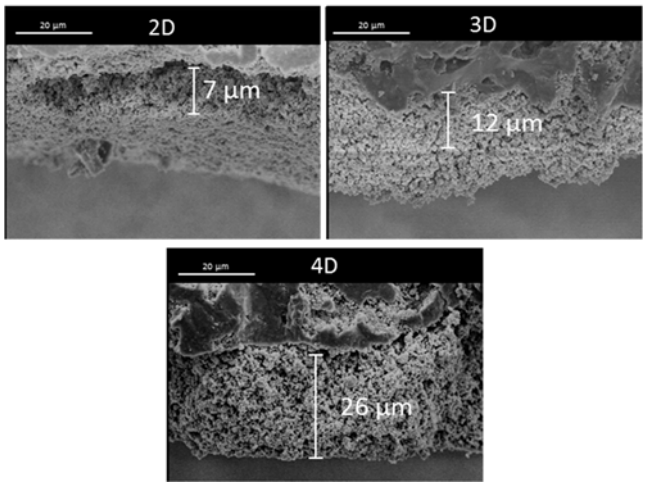

Figure 4: results of coating thickness fracture analysis

Results are in good accordance to the theoretical results reported in Figure 2-C. The pictures here reported are representative of a statistical SEM analysis performed on plenty of samples. It has to be stressed that considering monolith surface roughness, minor changes in local coating thickness are unavoidable. Anyway, the average value measured by SEM is in good accordance with the theoretical one. In addition to that, no detachment or adhesion problems between washcoat and substrate have been pointed out by the high magnification sampling obtained by SEM, even after the breakage of the sample to perform the analysis.

4. Conclusions

In this work, a new formulation was developed for low surface area cerium oxide dispersion and deposition. The use of a water-glycerol solution together with polyvinyl alcohol allowed to properly stabilize the powder dispersion. The resulting rheology curve obtained displayed both a shear-thinning behaviour suitable for dip coating deposition and viscosity values in the right range for washcoat deposition.
With the dip coating process used in order to perform depositions on ceramic monoliths, thin and homogeneous layers were washcoated on the support surface. Load and thickness were modulated by means of multiple dipping and values in line with what needed for catalytic testing were obtained.

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References

Agrafiotis C., Tsetsekou A. 2000. The effect of processing parameters on the properties of gamma-alumina washcoats deposited on ceramic honeycombs. *Journal of Materials Science,* 35**,** 951-960.
Cristiani C., Finocchio E., Latorrata S., Visconti C. G., Bianchi E., Tronconi E., Groppi G., Pollesel P. 2012. Activation of metallic open-cell foams via washcoat deposition of Ni/MgAl2O4 catalysts for steam reforming reaction. *Catalysis Today,* 197**,** 256-264.

Cristiani C., Valentini M., Merazzi M., Neglia S., Forzatti P. 2005. Effect of ageing time on chemical and rheological evolution in gamma-Al2O3 slurries for dip-coating. *Catalysis Today,* 105**,** 492-498.

Cristiani C., Visconti C. G., Finocchio E., Stampino P. G., Forzatti P. 2009. Towards the rationalization of the washcoating process conditions. *Catalysis Today,* 147**,** S24-S29.

Montebelli A., Visconti C. G., Groppi G., Tronconi E., Cristiani C., Ferreira C., Kohler S. 2014. Methods for the catalytic activation of metallic structured substrates. *Catalysis Science & Technology,* 4**,** 2846-2870.

Pino L., Vita A., Cordaro M., Recupero V., Hegde M. S. 2003. A comparative study of Pt/CeO2 catalysts for catalytic partial oxidation of methane to syngas for application in fuel cell electric vehicles. *Applied Catalysis a-General,* 243**,** 135-146.

Valentini M., Groppi G., Cristiani C., Levi M., Tronconi E., Forzatti P. 2001. The deposition of gamma-Al2O3 layers on ceramic and metallic supports for the preparation of structured catalysts. *Catalysis Today,* 69**,** 307-314.

Wu X. D., Weng D., Xu L. H., Li H. D. 2001. Structure and performance of gamma-alumina washcoat deposited by plasma spraying. *Surface & Coatings Technology,* 145**,** 226-232.

Zhang H., Suszynski W. J., Agrawal K. V., Tsapatsis M., Al Hashimi S., Francis L. F. 2012. Coating of Open Cell Foams. *Industrial & Engineering Chemistry Research,* 51**,** 9250-9259.