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Influence of γ -Al₂O₃ nano particles on the properties of washcoats deposited on cordierite monoliths

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The main aspects of washcoating of ceramic monolith by nano γ -Al₂O₃ slurry were studied. Some of the deposition characteristics of the washcoat such as morphology and homogeneity, specific load, thickness of the layer and adherence were examined. SEM was applied to assess the quality of the washcoat layer and measure its thickness. The adhesion of nano γ -Al₂O₃ washcoat on cordierite monolith was investigated by a vibrational ultrasonic and thermal shock tests. Nano γ -Al₂O₃ washcoat forms a good homogeneous layer on the monolith in comparison with the common micron size γ -Al₂O₃ particles, but some cracks appeared on washcoated layer.

Key words: Nano y-Al₂O₃, Washcoating, Cordierite monoliths, Loading percentage, Adhesion test, Morphology.

Introduction

Structured catalysts are currently applied in numerous chemical reactions because they have improved adequate efficiency in a variety of processes. These catalysts can be attractive replacements for conventional catalysts in slurry reactors or randomly packed beds [1]. Ceramic monoliths, a subgroup of structured catalysts, are among the most promising materials in removing the atmospheric pollutants, e.g. volatile organic compounds from the internal combustion engines [2-5] and the selective reduction of NO_x [1-3]. The monoliths are the best option when pressure drop, thermal or/and mechanical resistances are the key issues in the catalytic processes [6]. Cordierite monolith (a crystalline magnesium alumosilicate with hexagonal framework (2MgO.2Al₂O₃.5SiO₂) [7]) is the most consuming ceramic monoliths.

Cordierite monoliths have low surface area (usually $< 1 \text{ m}^2/\text{g}$); hence, it is necessary to coat them with a high surface area layer (carrier or secondary support) [8]. This layer is known as washcoat and can be an adequate bed for active phase deposition. Variety of properties such as high surface area, appropriate pore structure and high thermal stability of the washcoat layer are selected for evaluating the washcoating quality [9-11]. γ -Al₂O₃ is usually coated on the cordierite monolith [12] to produce a support that used in environmental applications, chemical and construction processes such as three-way catalyst supports (known as TWC) [13]. Commercial submicron γ -Al₂O₃ powder is commonly

used in washcoating the monoliths [14].

Different methods and techniques have been proposed for manufacturing monolithic catalysts [1, 6, 15, 16]. Coating through the medium of a slurry, commonly called washcoating, is the most popular and usual technique [2]. In this method, a slurry with different macro particles is used [17]. Agrafiotis and Tsetsekou reported that in washcoat preparation, some properties of the solution (such as stability and rheological properties) should be optimized. In this manner, a uniform layer of washcoat on monolith surface is formed [18]. Leenaars and Burggraaf proposed two mechanisms for formation of the coating layer on support surface [19]. In the first mechanism, where capillary suction is predominant, capillary forces drive the suspension of alumina into the support. In the second mechanism, known as filtration, a cake film begins to form on the support wall. The difference between the two mechanisms is significant. If particle size of the solved powder is very small, the latter is the main mechanism. However, the quality of the deposited washcoat is affected by some properties such as the nature and particle size of alumina, concentration of alumina solution etc.

Some investigators have proposed the γ -Al₂O₃ powder, with the mean particle size of 3 to 10 microns, for monolith washcoating [18, 20, 21]. The stabilization of γ -Al₂O₃ particles is necessary to prevent the Van der Waals forces which cause particle aggregation which affects the adherence between the coating and the substrate [22]. To obtain the stable slurries, different particle size distributions of solids below 10 µm have been proposed [20, 23]; while there exists no report on the effect of nano sized γ -Al₂O₃ on washcoated layer efficiency.

Preparation and characterization of nano size γ -Al₂O₃ washcoated on cordierite monolith is focused in this

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study. To obtain a mechanically stable washcoat, the adhesion of the washcoat was evaluated by applying the vibrational ultrasonic and the thermal shock techniques.

Experimental Procedure

Washcoating of monoliths

The cordierite ceramic used in this study (purchased from Iran Delco) is a commercial product with 540 cells per square inch (cpsi) and has a BET surface area of $0.7 \text{ m}^2/\text{g}$. Geometric parameters of this raw monolith are presented in Table 1. Before the coating process, the raw cordierite monoliths were washed for 15 minutes with acetone and dried in an oven for 30 minutes at 110 °C to remove the superficial impurities. Acid treatment was carried out to increase the surface area of monoliths and washcoat adhesion as well. For this purpose, these monoliths were first floated in nitric acid solution for 15 minutes, next dried at 100 °C in the oven for 30 minutes and finally calcinated at 560 °C for one hour in a furnace.

The monoliths were washcoated with aqueous suspensions of 15, 20, 30 and 35 wt% nano γ -Al₂O₃ solutions. These solutions were prepared by dissolution of certain amounts of nano γ -Al₂O₃ powder (Kimiazi Institute, Iran, $d_{50} = 50$ nm) in distilled water. These solutions were stirred vigorously for 24 hours. The appropriate amounts of acid (HCl) and base (NaOH) were added to adjust pH and stabilize the slurry [18].

This washcoating procedure included three steps: (1) the raw monoliths were dipped vertically into nano \tilde{a} -Al₂O₃ solution for 5 minutes, (2) the dipped monoliths were withdrawn and exposed to air flow for removing excess suspension and (3) the monoliths were dried at 110 °C for 1.5 hour in an oven and then calcinated for 2 hours at 560 °C in a furnace. This procedure was repeated only once. The load of deposited coating was determined gravimetrically, according to eq. (1);

Loading % =
$$\frac{m_{\text{coated}} - m_0}{m_0} \times 100$$
 (1)

where, m_{coated} is the weight of washcoated monolith after calcination and m_0 is the weight of uncoated monolith.

Adhesion test

Adhesion of washcoat on surface of monoliths

 Table 1. Geometric parameters of the monolith used.

Description	Values
Wall thickness	0.279 mm (0.011 in.)
Cell spacing	1.092 mm (0.043 in.)
Geometric surface area	2.71 mm ² /mm ³ (69.12 in ² /in ³)
Open frontal area	0.752
Hydraulic diameter	0.787 mm (0.031 in.)

(mechanical stability) was evaluated by two different methods:

1) The ultrasonic bath [14], where the monoliths were immersed in ethanol and exposed to high frequency ultrasonic wave (40 KHz). The weight losses were monitored in 30 minute intervals at six steps.

2) The thermal shock [24], where the monoliths were heated up to 350 °C in furnace for 30 minutes and then put in a cold box at -8 °C for 5 minutes. This procedure was repeated five times and then weight loss was measured.

These two types of testing are adequate in studying the strength and adhesion of washcoat for a wide range of monolith applications. The loss percentage in both the methods was calculated according to eq. (2):

Loss percentage of washcoat =
$$\frac{m_{\text{final}} - m_{\text{initial}}}{m_0} \times 100$$
 (2)

where, $m_{\text{final step}}$ is the final weight of washcoated monolith and m_{initial} is the weight of washcoated monolith before test.

Characterization methods

The XRD characterization was performed with X-ray diffractometer (Philips D6792) using a copper target at 40 kV \times 100 mA at room temperature and 8 min⁻¹ scanning speed. Scanning Electron Microscopy (Philips XL30 ESEM) was used to studding the morphology of the coated specimens and the quality of the deposited layer. The coating thickness was measured by SEM as well. Prior to SEM analysis, the samples were coated with a thin conductive layer of gold.

Results and Discussion

XRD analysis

The result of XRD analysis for washcoated monolith is shown in Fig. 1. The analysis indicates the presence of cordierite phase in the washcoated monolith. The characteristic peaks for cordierite appeared in the XRD pattern. The most intense peaks at $2\theta = 10.0$, 21.2, 26.5, 28.5 and 29.5 can be attributed to the cordierite [25]. It is worth mentioning that there are no significant peaks for alumina in the pattern. Crystalline alumina is not found in the sample, indicating that amorphous structures or very small crystallites are obtained. It seems that alumina is well dispersed as small crystallites. The size of nano γ -Al₂O₃ particles was estimated by Scherrer equation. The average crystal size was in 18-35.3 nm range.

Morphology of washcoat

The morphology of raw monolith and washcoated with nano γ -Al₂O₃ are shown in Fig. 2(a-e). All these monoliths were washcoated through one step coating. The Fig. 2(b-e) represents the comparison of monoliths coated with slurries of different solid contents of nano



Fig. 1. XRD pattern of washcoated monolith compared with alumina and raw monolith (\bullet : cordierite, \blacktriangle : alumina).



Fig. 2. SEM images of the monolithic channels with one step coating. (a) raw monolith (without coating), (b) washcoated with 15 wt.% slurry, (c) washcoated with 20 wt.% slurry, (d) washcoated with 30 wt.% slurry, and (e) washcoated with 35 wt.% slurry.

 γ -Al₂O₃ (15, 20, 30 and 35 wt.%). It is clear that in any channel, the washcoat thickness is maximum at the corners and minimum at the sides. A homogeneous washcoat layer onto the monolith walls was obtained. Because cordierite monoliths contain many macro pores [26], when the raw monolith is dipped into nano y-Al₂O₃ slurry, most of the macro pores of monolith can be filled with the slurry; this is due to the interaction between monolith and washcoat [17]. In other words, accessibility of washcoat depends strongly on particle size of γ -Al₂O₃ powder used in slurry preparation. When the particle size reduces, it leads to more diffusion of γ -Al₂O₃ from washcoat slurry to monolith pores which reduces the accessibility of washcoat on the monolith surface. The coatings of nano γ -Al₂O₃ with different concentrations not more than 30 wt.% were homogeneous. An increase in solids concentration in the slurry beyond 30 wt.% resulted in lack of homogeneity and the development of cracks.



Fig. 3. Cracks on the surface of washcoat.



Fig. 4. SEM images of the monolithic channels with two steps of impregnation: (a) washcoated with 15 wt.% slurry, (b) washcoated with 20 wt.% slurry, (c) washcoated with 30 wt.% slurry (d) washcoated with 35 wt.% slurry.

The ultimate objective of the deposition process is to obtain a uniform washcoat layer. As illustrated in Fig. 2(b-e), an increase in nano γ -Al₂O₃ concentration of slurry leads to an increase in non-uniformity in the washcoat layer. Therefore, the washcoating with nano γ -Al₂O₃ slurries yields more uniformity than slurries with larger particle size. A coating of sufficient loading and thickness may influence on active phase deposition and then on the catalytic performance.

As it is represented in Fig. 3, there are some cracks in a few areas of washcoat, mainly in the most external coating layer. There are two reasons for this phenomenon: 1) the thermal processes (calcination and drying) need to remove the solvent from the slurry. Evaporation and escape of solvent from washcoat and monolith pores cause expansion and cracks on the outer layer of washcoat. Also a difference in thermal expansion between the cordierite and γ -Al₂O₃ promotes cracking in washcoat; 2) the adhesion of different layers of nano γ -Al₂O₃ on monolith surface. Since there are high repulsive forces between nano γ -Al₂O₃ layers, the adhesion is weak. It is shown in Fig. 3 (right image), that cracks are formed when the washcoat thickness is relatively high. This high thickness causes an increase in crack formation and a poor coating adherence. The presence of cracks is a main disadvantage in washcoat layer because the coatings would have low mechanical resistance, which leads to a peel off under rigorous conditions [27]. The presence of cracks in the coating layer confirms that the stresses generated on the layer during drying were thick enough to generate shrinkages [28, 29].

The SEM images of the monoliths coated with two steps dipping have been presented in Fig. 4(a-d). As observed clearly, there is a uniform washcoat in monolith walls coated with 15 wt.% solid content slurry. Moreover, an increase in solid content leads to an increase in washcoat layer thickness and a reduction in uniformity. Cracking of washcoat occurs especially when 30 and 35 wt.% precursor slurries are used.

Effect of solid content

The solid content of solution has a direct influence on viscosity of suspension. Although, the penetration in channels of monoliths is difficult in high viscous slurry, high loading of washcoat per coating step is inevitable. The percentage of loading per solid content of nano γ -Al₂O₃ solution in one and two steps coating is illustrated in Fig. 5.

The dependency of the thickness of the deposited layer on the solid content of nano γ -Al₂O₃ suspension is shown in Fig. 6. An increase in the slurry solids concentration leads to more particles be attachment onto the monolith surface, hence, an increase in washcoat thickness. A smooth coating layer with about 5-18 µm thickness was obtained on the external channel surface of the monolith coated with one step coating. This thickness range increases to 9-34.7µm



Fig. 5. Loading percentage of washcoat at different solid contents of nano γ -Al₂O₃ solution.



Fig. 6. The dependency of the thickness of the deposited layer on the solid content of suspension.

when two steps coating was applied. Increasing the washcoat thickness is necessary to performance the activity of the active phase that would be deposited on the washcoat [27]. Thicker in washcoat leads to provide inadequate area for deposition of active phase, because it will not be able to cover the whole surface of the monolith. Instead, higher thickness of washcoat leads to a decrease in available surface for deposition of active phase. Moreover, thickness has an influence on flow regime within the channels and enhances pressure drop.

Adhesion test

The adhesion characteristics depend strongly on the washcoat slurry powder particle size [20]. Agrafiotis and Tsetsekou reported that a reduction in powder particle size reduces the washcoat weight loss. They observed that washcoat with 2 μ m particle size has less weight loss in comparison to washcoats with 6, 17 and 52 μ m particle size [18]. They did not refer to or study the effect of γ -Al₂O₃ powder with particle size less than 2 μ m especially nano γ -Al₂O₃.

The weight loss of washcoated monoliths with solid content of nano γ -Al₂O₃ under standard ultrasound test conditions is shown in Fig. 7. Here, an increase in the solid content from 15 wt.% to 20 wt.% leads to the weight loss form ~16 to ~53 wt.%. This loss increases to ~69 wt.% by an increase in the slurry solid content at 35 wt.%. Whereas the weight loss of washcoat with 35 wt.% solid content and particle size of 2 µm is about 3.8 wt.% [20]. This might be due to more



Fig. 7. Washcoat loss percentage in different solid contents of nano γ -Al₂O₃ solution in vibrational ultrasonic test.



Fig. 8. Washcoat loss (wt.%) in different solid content of nano γ -Al₂O₃ solution in thermal shock test.

repulsion force between γ -Al₂O₃ nano particles, or it might be due to the cracks in the washcoat surface. It is expected that poor adhesion leads to high loss of washcoat which is directly related to solid content of nano γ -Al₂O₃ slurry. Less concentration of nano γ -Al₂O₃ in the slurry (with low viscosity) causes more penetration of γ -Al₂O₃ into the pores, hence, less washcoat loss. It is supposed that a weak adhesion of nano γ -Al₂O₃washcoat layers with monolith walls can amplify washcoat loss.

Mechanical stability of the washcoat in monoliths is a critical issue for application purposes where coating loss could be completely avoided. These washcoated monoliths do not show good stability of the coating since a high weight loss was measured after the ultrasound test. However, this washcoat is not firmly attached to monolith and is not mechanically stable. It is proposed that using some binders consisting of different oxides (alumina, silica) or precursors of them as metal nitrates can improve the coating adherence [30].

The resistance of the washcoated monolith to thermal shock is shown in Fig. 8. It is clear that weight losses increase with an increase in solid content of slurry. There is just a 1.1 wt.% loss in washcoat with 15 wt.% solid content slurry. This loss increases to about 16 wt.% by increasing the solid content to 35 wt.%. As Chen et al. described, the difference between thermal expansion coefficients of the monolith and washcoat leads to their different expansion quantities [31]. This thermal shock (hot and cold) results in spallation of the washcoat layer. Generally, compared with results obtained in published articles, nano y-Al₂O₃ washcoat has more loss than washcoats with particle size in 2 to 10 im range [20, 23]. This results from low adhesion of nano γ -Al₂O₃ on monolith surface and low adhesion between washcoat layers.

When a monolithic catalyst is heated or cooled, the difference between thermal expansion coefficients of the washcoat and cordierite leads to their different expansion quantities which causes stress concentration at their interface, where the thermal stress is induced. This phenomenon may result in the spallation of the washcoat layer [31].

Conclusions

Influence of γ -Al₂O₃ nano particles on the properties of washcoats deposited on cordierite monoliths was examined comprehensively. In order to analyze the significant aspects of γ -Al₂O₃ nano particles, it is important to compare the results of this study with γ -Al₂O₃ micro particles. The results of the experiments indicated that the size of adopted particles concur with quality of production, especially the characteristics of the results and properties of washcoats deposited on ceramic monoliths. Here, just like other technical experiments, the coating of cordierite monolith with nano γ -Al₂O₃ slurries was investigated to achieve the desired washcoat quality. The thickness of this adhered layer increases with an increase in solid content of solution and repeating the number of coating (washcoating). An increase in thickness has some advantages (such as formation of homogeneous layer on the monolith) in application of nano particles rather than the common size utilized for coating monolith and some disadvantages such as generation of some cracks on first washcoated layer.

References

- 1. A. Cybulski and J.A. Moulijn., "Stuctured catalysts and reactors", (New York: Marcel Dekker, Inc. 1998).
- B.P. Barbero, L. Costa-Almeida, O. Sanz, M.R. Morales, L.E. Cadus and M. Montes, Chem. Eng. J. 139 (2008) 430-435.
- J. Adler, Int. J. Appl. Ceram. Technol. 2 [6] (2005) 429-439.
 T. Paramadayalan and A. Pant, Korean J. Chem. Eng. 30
- [12] (2013) 2170-2177.
- D. Fino, P. Fino, G. Saracco and V. Specchia, Korean J. Chem. Eng. 20 [3] (2003) 445-450.
- P. Avila, M. Montes and E.E. Mirò, Chem. Eng. J. 109 (2005) 11-36.
- 7. I. Santacruz, R. Moreno and J.B.R. Neto, Int. J. Appl. Ceram. Technol. 5 [1] (2008) 74-83.
- C. Agrafiotis and A. Tsetsekou, J. Eur. Ceram. Soc. 22 (2002) 423-434.
- 9. C. Morterra and G. Magnacca, Catal. Today, 27[3-4] (1996) 497-532.
- L.D. Hart and E. Lense, "Alumina chemicals: science and technology handbook The American Ceramic Society", (Westerville, Ohio: Wiley 2006).
- 11. A.K. Mogalicherla and D. Kunzru, Int. J. Appl. Ceram. Technol, 8 [2] (2011) 430-436.
- K.P. Goodboy and J.C. Downing, "Production, processes, properties and applications for activated and catalytic aluminas". Alumina Chemicals : Science and Technology Handbook, ed. L.D. Hart. (The American Ceramic Society Inc, Westerville OH, USA1990).
- 13. J.L. Williams, Catal. Today. 69 (2001) 3-9.
- M. Valentini, G. Groppi, C. Cristiani, M. Levi, E. Tronconi and P. Forzatti, Catal. Today, 69 (2001) 307-314.
- 15. V. Meille, Appl. Catal., A, 315 [(2006) 1-17.
- D. M. Frías, S. Nousir, I. Barrio, M. Montes, L. M. Martínez, M. A. Centeno and J. A. Odriozola, App. Catal. A., 325 (2007) 205-212.
- T. A. Nijhuis, A. E. W. Beers, T. Vergunst, I. Hoek, F. Kapteijn and J. A. Moulijn, Catal. Rev., 43 [4] (2001) 345-380.
- C. Agrafiotis and A. Tsetsekou, J. Eur. Ceram. Soc., 20 [(2000) 815-824.
- A. F. M. Leenaars and A. J. Burggraaf, J. Colloid Interf. Sci., 105 [1] (1985) 27-40.
- C. Agrafiotis, A. Tsetsekou and A. Ekonomakou, J. Mater. Sci. Lett., 18 [17] (1999) 1421-1424.
- 21. C. Agrafiotis and A. Tsetsekou, J. Mater . Sci., 35 (2000) 951-960.
- 22. J. Davies and J. G. P. Binner, J. Eur. Ceram. Soc., 20 [10] (2000) 1539-1553.
- J.R. González-Velasco, M.A. Gutiérrez-Ortiz, J.L. Marc, J.A. Botas, M.P. González-Marcos and G. Blanchard, Ind. Eng. Chem. Res. 42 [2] (2003) 311-317.
- 24. S. Zhao, J. Zhang, D. Weng and X. Wu, Surf. Coat.

Technol. 167 [1] (2003) 97-105.

- A. Bueno-López, D. Lozano-Castelló, I. Such-Basáñez, J.M. García-Cortés, M.J. Illán-Gómez and C.S.-M. d. Lecea, App. Catal. A. 58 (2005) 1-7.
- 26. L. Villegas, F. Masset and N. Guilhaume, Appl. Catal. A 320 (2007) 43-55.
- 27. A.K. Mogalicherla and D. Kunzru, Chem. Eng. Res. Des. 88 (2010) 1057-1066.
- W. Fei, S.C. Kuiry, Y. Sohn and S. Seal, Surf. Eng., 19 [3] (2003) 189-194
- P. O. Thevenin, A. G. Ersson, H.M. J. Kušar, P.G. Menon and S.G. Järås, App. Catal. A. 212 [1-2] (2001) 189-197.
- A.V. Boix, E.E. Miró, E.A. Lombardo, R. Mariscal and J.L.G. Fierro, App. Catal. A. 274 (2004) 197-205.
- 31. H. Chen, J. Wang, H. Li, D. Wu, M. Yao and Y. Li, App. Catal. A. 427-428 (2012) 73-78.