Mechanical Stability of Monolithic Catalysts: Factors Affecting Washcoat Adhesion and Cohesion During Preparation

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DOI 10.1002/aic.14480

Alumina-washcoated cordierite monoliths are prepared to investigate the effects of the preparation process factors on the mechanical stability of monolithic catalysts. It is shown that the agent for pretreating substrates, properties of the washcoating solution (solid content, additive, and amount of additive), and washcoating times all have great effects on the washcoat loading and on the washcoat adhesion and cohesion. There is a great possibility of improving the mechanical stability through the optimization of these factors. If multiple washcoating is performed, the two-time washcoating after calcination is recommended in this case. It is also pointed out that the minor variation of the washcoat loading with monolithic mini-specimen increases the scatter of the washcoat adhesion and cohesion, resulting from fatigue failure of active material. Furthermore, the previously proposed mechanical failure mechanism is confirmed to be an effective tool to factors analysis of the mechanical stability of cordierite monolithic catalysts. © 2014 American Institute of Chemical Engineers *AIChE J*, 60: 2765–2773, 2014

Keywords: monolithic catalyst, catalyst preparation, factor analysis, mechanical stability, washcoat adhesion, washcoat cohesion

Introduction

Development of monolithic catalysts and reactors has been one of the major achievements in the field of heterogeneous catalysis and catalytic reaction engineering.[1–11] In industrial applications, monolithic catalysts may experience various damaging stresses, for example, thermal, chemical, and mechanical stresses, especially during many rapid changes in operating conditions. These stresses probably result in the mechanical failure of monolithic catalysts, that is, spalling (loss) of the active material washcoated on the monolithic substrate, causing degradation of catalyst efficiency and potential damage for downstream equipment.[1–3,12,13] The mechanical integrity and stability of monolithic catalysts are, therefore, one of the key parameters for the reliable and efficient performance of industrial monolithic reactors.[13]

Academic institutions active in catalysis research generally concentrate on the chemistry rather than the catalyst mechanical properties. Few articles choosing the mechanical stability of monolithic catalysts as the subject investigated are, therefore, available in the open literature, although the washcoat adhesion is tested and evaluated in almost all publications on monolithic catalysts.[14–31] Mitra and Kunzru[25] washcoated cordierite monoliths with different zeolite powders and claimed that the washcoat adhesion and loading depend on the nature of the powder as well as the properties of the slurry. Zamaro et al.[27,28] found a good correlation between zeolite particle size and adhesion of zeolite washcoat to cordierite honeycombs, the lower the particle dimension the higher the mechanical stability of the washcoat layer. Agrafiotis et al.[14–16] reported that the adhesion of alumina washcoat to cordierite monoliths is due to the interlocking of washcoating particles, and the reduction of particle size to colloidal dimension is essential for a well-adhered washcoat. Chen et al.[29] stated that the calcination temperature has a great effect on the adhesion strength of the Hopcalite washcoat and that the solid reaction between the Hopcalite washcoat and cordierite monolith improves the washcoat adhesion. Zhao et al.[30] proposed that a well-adhered γ-alumina washcoat layer can be formed on FeCrAl metallic substrate using a three-step method, that is, preoxidation, primer deposition and coating deposition. Zhang et al.[31] examined the effect of different intermediate materials on the adhesion of hexaaluminate to metallic substrate, and pointed out that the hexaaluminate adhesion could be improved by the introduction of an alumina intermediate layer. Furthermore, it was widely reported that the washcoat adhesion can be improved by appropriate additives/binders such as alumina and silica (ceramic monoliths)[20,22,26] or by appropriate thermal and/or chemical pretreatments of metal surface (metallic monoliths).[18,19,23,32,33]

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Table 1. Prepared Catalyst Samples and Their Weight Losses Due to Ultrasonic Treatment

Sample	Bare Monolith Weight, $\bar{m}_{\mathrm{sub}}$ (g/monolith)	Washcoat Loading		Loss of Weight	
		$\overline{\Delta m}_{\mathrm{wash}}$ (g/monolith)	l (wt %)	$\overline{\Delta m}_{\mathrm{ultr}}$ (g/monolith)	w (wt %)
1	0.5574	0.0555	10.0	0.0113	20.3
2	0.5369	0.0545	10.2	0.0099	18.1
3	0.5330	0.0641	12.0	0.0156	24.3
4	0.5526	0.0287	5.2	0.0021	7.2
5	0.5417	0.0612	11.3	0.0086	14.1
6	0.5452	0.0647	11.9	0.0077	11.9
7	0.5505	0.0743	13.5	0.0081	11.0
8	0.5155	0.0554	10.7	0.0102	18.4
9	0.5070	0.0750	14.8	0.0058	7.8
10	0.5145	0.0794	15.4	0.0076	9.6
11	0.5423	0.0955	17.6	0.0144	15.0
12	0.5502	0.1401	25.5	0.0146	10.4
13	0.5463	0.1537	28.1	0.0276	18.0
14	0.5481	0.2716	49.6	0.0815	30.0

In previous publications from this group, it has been shown that the spalling of active material includes adhesive failure (interface spalling), where failure occurs at the washcoat layer-cordierite substrate interface, and cohesive failure (interior spalling), where failure occurs within the washcoat layer.[13] The mechanical stability of cordierite monolithic catalysts, therefore, involves a combination of the washcoat adhesion and cohesion. It has also been proposed that the mechanical failure of cordierite monolithic catalysts is a random stress-induced fatigue damage process, that is, microcracks are first initiated at the preexisting flaws and then propagate to form macrocracks, leading to the washcoat surface cracking, interconnection between large cracks, and consequent spalling of active material.[13] Thus, it can be seen that the mechanical stability of monolithic catalysts is highly dependent on the material properties and microstructures of the washcoat layer and its interface with the monolithic substrate. During catalyst manufacturing, various process factors (parameters) will have effects on these material properties and microstructures, and in consequence on the mechanical stability of monolithic catalysts. It is, therefore, important for catalyst developers to analyze and optimize the manufacturing process factors for improving the mechanical stability of monolithic catalysts.

It is crucial that the washcoat layer adheres well to the monolithic substrate to prevent spalling. The primary objective of this article is to investigate the effects of the preparation process factors on the washcoat adhesion and cohesion, and to demonstrate the possibility of improving the mechanical stability of an alumina-washcoated cordierite monolithic catalyst during preparation. The relationship between the process factors and the mechanical stability was also explained based on the previously proposed mechanical failure mechanism of cordierite monolithic catalysts.[13]

Experimental

Preparation of monolithic catalysts

Cylindrically shaped monolithic structures (Φ 8 × 24 mm) were obtained by cutting commercial cordierite straight-channel monoliths with a square cell density of 400 cpsi (cells per square inch) and a wall thickness of 0.21 mm. Before use, these mini-monoliths were immersed in a pretreating agent for 1 h and then calcined at 600°C in air for 2 h to remove adsorbed impurities. The pretreated monolith channel walls were observed by a FEI Sirion 200 field-emission scanning electron microscope.

A stable alumina sol was prepared from a mixture of pseudoboehmite and deionized water. In some cases, an additive was also added. The mixture was vigorously stirred at 80°C for 1 h. In this period, a small amount of nitric acid was added slowly to maintain pH at 2.0. The weight ratio of pseudoboehmite to deionized water was, hereafter, referred to as the solid content, and the amount of additive (if any) was defined as the weight of additive divided by the total weight of pseudoboehmite and deionized water.

Dried mini-monoliths were dipped in this sol for approximately 1 min. They were then taken out and shaken, and the excess liquid still remaining in the channels was gently blown out using compressed air. Afterward, the coated monoliths were left horizontally and dried at 120°C in air for 1 h, followed by calcination at 600°C in air for 3 h. If the washcoating process needed to be carried out several times, two ways were adopted. One was by multiple washcoating after drying, that is, dipping was performed repeatedly after drying and the coated monoliths were finally calcined. The other was by multiple washcoating after calcination, that is, dipping was performed repeatedly only after calcination.

Analysis of preparation factors

In the preparation of monolithic catalysts, there are many process factors which have possible effects on the mechanical stability of monolithic catalysts, for example, the agent used for pretreating monolithic substrates, solid content, additive, amount of additive, washcoating times, drying temperature and time, and calcination temperature and time. In this study, the first five factors were selected as controllable factors to examine the effect of the preparation process on the adhesion and cohesion of the washcoated active material. For this purpose, a total of 14 samples were prepared under different conditions and listed in Table 1. Each sample was comprised of five monolithic catalyst specimens prepared under the same conditions. In relative terms, the loadings of active material (γ-alumina washcoat layer) for individual specimens and individual samples, l_i and l, were determined, respectively, with

$$l_i=\frac{\Delta m_{\mathrm{wash},i}}{m_{\mathrm{sub},i}}=\frac{m_{\mathrm{wash},\ i}-m_{\mathrm{sub},i}}{m_{\mathrm{sub},i}}\times 100\% \tag{1}$$

$$l=\frac{\overline{\Delta m}_{\mathrm{wash}}}{\bar{m}_{\mathrm{sub}}}=\frac{\sum_{i=1}^{5}\left(m_{\mathrm{wash},i}-m_{\mathrm{sub},i}\right)}{\sum_{i=1}^{5}m_{\mathrm{sub},i}}\times 100\% \tag{2}$$

where $m_{\mathrm{sub},i}$ is the initial weight of the ith monolithic substrate, $m_{\mathrm{wash},i}$ the weight of the ith washcoated monolith

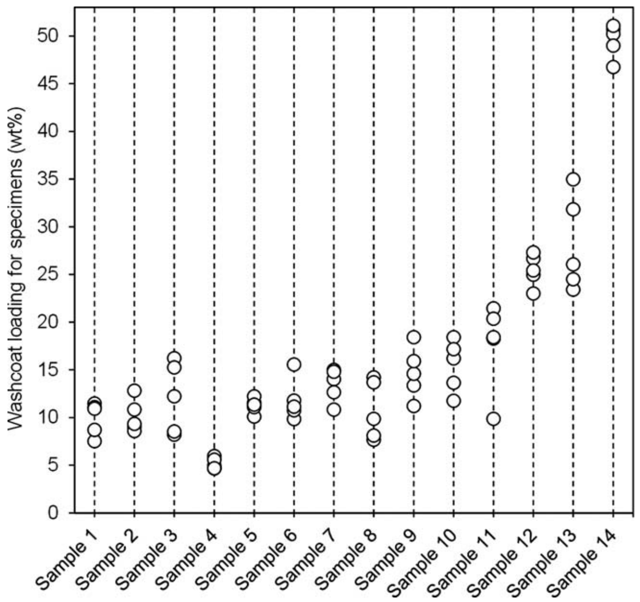

Figure 1. Scatter of the washcoat loading data of monolithic specimens.

(specimen), $\Delta m_{\mathrm{wash},\ i}$ the washcoat weight of the ith specimen, $\bar{m}_{\mathrm{sub}}$ the mean of the initial weights of five substrates, and $\overline{\Delta m}_{\mathrm{wash}}$ the mean of the washcoat weights of five specimens, which is treated as the washcoat loading, expressed in an absolute term, for a sample.

Determination of mechanical stability

The washcoat adhesion and cohesion were measured in terms of its resistance to ultrasonic vibration.[18–31] Monolithic catalysts were immersed in petroleum ether inside test tubes, and then treated in an ultrasonic bath (40 Hz/60 W) for 30 min. The specimens were taken out, dried, and weighed. In relative terms, the losses of weight for individual specimens and individual samples, w_i and w, were calculated, respectively, with

$$w_i=\frac{\Delta m_{\mathrm{ultr},i}}{\Delta m_{\mathrm{wash},i}}=\frac{m_{\mathrm{wash},i}-m_{\mathrm{ultr},i}}{m_{\mathrm{wash},i}-m_{\mathrm{sub},i}}\times 100\% \tag{3}$$

$$w=\frac{\overline{\Delta m}_{\mathrm{ultr}}}{\overline{\Delta m}_{\mathrm{wash}}}=\frac{\sum_{i=1}^{5}\left(m_{\mathrm{wash},\ i}-m_{\mathrm{ultr},i}\right)}{\sum_{i=1}^{5}\left(m_{\mathrm{wash},i}-m_{\mathrm{sub},i}\right)}\times 100\% \tag{4}$$

where $m_{\mathrm{ultr},i}$ is the weight of the ith specimen after ultrasonic treatment, $\Delta m_{\mathrm{ultr},i}$ the decrease in the weight of the ith specimen due to ultrasonic treatment, and $\overline{\Delta m}_{\mathrm{ultr}}$ the mean of the weight reductions of five specimens, that is, the loss of weight, expressed in an absolute term, for a sample.

Results and Discussion

Catalyst specimens, samples, and mechanical stabilities

Table 1 gives a description of the chemical compositions and ultrasonic vibration resistances of the prepared catalyst samples. The washcoat loading and weight loss for individual monolithic specimens are presented in Figures 1 and 2, respectively.

As can be seen from Figure 1, for any sample, the washcoat loading changes with specimen in a certain range, although the five catalyst specimens have the same geometrical size, and were prepared under the same conditions and by the same method. In this figure, the washcoat loading is expressed as the washcoat weight divided by the substrate weight, as given in Eq. 1. Alternatively, the washcoat loading is sometimes defined as the washcoat weight divided by the substrate volume; however, similar variation also exists in the washcoat loading defined in this way. One of the possible reasons for the variation is that there exist some minor discrepancies in the channel walls of individual cordierite mini-substrates, for example, surface roughness. Furthermore, an inaccurate control of preparation also leads to the scatter of the washcoat loading. For instance, the removal of the excess liquid by compressed air is one of the key steps related to the washcoating of active material. The distance between specimen and air knife, airflow direction, and blowing time all have effects on the washcoat loading, and thus, the unconscious changes in these factors may cause differences between monolithic specimens. Mini-monoliths are usually used in laboratory studies of monolithic catalysts, and the minor variability of their washcoat loadings is inevitable. Therefore, a selection procedure has to be performed if approximate loadings of washcoat are required for individual specimens.

Figure 2 shows that the loss of weight for specimens scatters in a much larger range, compared to the washcoat loading. In this study, 30 min of ultrasonic vibration was carried out. As the vibration time increases, the loss of weight for specimens will increase; however, the scattering property of the weight loss data always exists regardless of ultrasonic conditions.[13] As mentioned above, the mechanical failure of cordierite monolithic catalysts is a random stress-induced fatigue damage process.[13] There exist various flaws, for example, pores, crystal edges, grain boundaries, interphase boundaries, and dislocations, within the washcoat layer and at the washcoat layer-cordierite substrate interface. The random variation of size, shape, and orientation of these flaws with specimen leads to the random variation of fatigue damage, and thus to the large scatter of the weight loss data. Therefore, the weight loss of monolithic mini-catalysts is distributed over a wide range of values, even if a set of

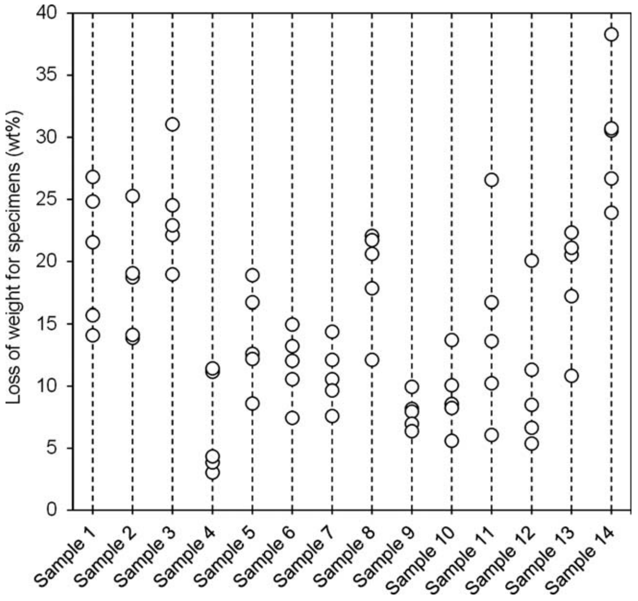

Figure 2. Scatter of the weight loss data of monolithic specimens.

nominally identical specimens (with the same geometrical size, active material loading, and preparation history) is measured by ultrasonic vibration under the same conditions.[13] In addition, the washcoat loading variation will add cause for the scatter of the weight loss for specimens. Generally, the higher the washcoat loading, the larger the weight loss will be, which is detailedly elucidated below.

Mini-monoliths used in laboratory studies are generally obtained by cutting commercial large-sized monoliths. After washcoating of active material, monolithic catalyst mini-specimens are produced. A combination of a lot of these mini-specimens can be considered to form a large-sized monolithic catalyst, and the purpose of studying mini-specimens is, therefore, to try to explore the performance of the large-sized catalyst. Nevertheless, the mini-specimens prepared under the same conditions have slightly different washcoat loadings and significantly different losses of weight, all of which are not due to experimental noise. It reveals that the large-sized catalyst sample cannot be represented by any single mini-specimen. An accurate description of the large-sized sample should take all the mini-specimens into consideration. For instance, the weight losses of all the mini-specimens are summed or averaged to give a reliable mechanical stability of the large-sized sample. Furthermore, the larger the number of the examined mini-specimens, the more accurate the catalyst properties obtained will be. For any small number of specimens, only an estimate can be achieved. However, in practice, a small number of specimens are expected because of the saving of labor and material. In this study, five monolithic specimens were prepared and measured for each sample, and then, the averages of their washcoat loadings and weight losses were calculated by Eqs. 2 and 4 and used as the reliable chemical compositions and mechanical stabilities of the catalyst samples, listed in Table 1.

It should be reaffirmed that the purpose of summing/averaging the measured mini-specimen properties is not to make a statistical analysis but to perform the scale-up from mini-specimens to a large-sized catalyst sample. As stated above, the large-sized sample cannot be represented by any single mini-specimen due to the inherent variations in the washcoat loading and weight loss. It reveals that any statistical analysis of the mini-specimen properties is meaningless in this case.

Effect of the pretreating agent

In the literature,[12,34–36] water, acetic acid, and nitric acid were usually used to pretreat cordierite monolithic substrates. Using them, three samples were prepared in this study to examine the effects of the pretreating agent on the washcoat loading and on the washcoat adhesion and cohesion, and the results are presented in Figure 3. As shown in Table 1, the bare monolith weight, $\bar{m}_{\text{sub}}$, remains approximately constant, and thus, the washcoat loading expressed in a relative term, l, is in direct proportion to that expressed in an absolute term, $\overline{\Delta m}_{\text{wash}}$. For ease of analysis, in Figure 3 the washcoat loading is plotted only in an absolute term as the weight loss due to ultrasonic treatment is directly related to the absolute washcoat loading and not to the relative washcoat loading. It can be seen that the pretreatment with 50 wt % nitric acid gives not only the highest washcoat loading but also the largest loss of weight. And the pretreatment with 50 wt % acetic acid leads to the smallest loss of weight, although it is very similar to the pretreatment with distilled water in the washcoat loading.

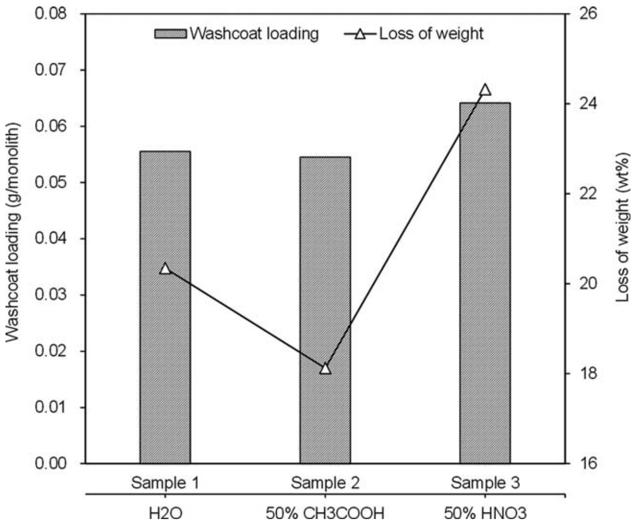

Figure 3. Influence of the pretreating agent on the washcoat loading and on the washcoat adhesion and cohesion (Preparation conditions: solid content of 20 wt %, no additive, single washcoating).

As mentioned afore, the spalling of active material includes adhesive failure and cohesive failure, and the mechanical stability of cordierite monolithic catalysts involves a combination of the washcoat adhesion and cohesion.[13] Clearly, the cordierite pretreatment has a possibly direct effect on the properties of the flaws at the washcoat layer-cordierite interface, and thus will have an effect on the washcoat adhesion.

Figure 4 shows the scanning electron microscope (SEM) images of the cordierite monoliths pretreated by the three agents and without pretreatment. Both distilled water and acetic acid have no obviously corrosive action to the cordierite ceramic material, and their treatments cannot change the surface structures of monolithic substrates, thus leading to the fact that the substrates pretreated by the two agents give similar washcoat loadings. However, compared to distilled water, acetic acid can effectively remove grease and dust particles adhering in grease, and thus gives a much cleaner substrate surface, as shown in Figure 4. The washcoat layer interacts more closely with the clean monolithic substrate, which increases the washcoat adhesion and, then, reduces the amount of adhesive failure. As a result, the substrate pretreated by acetic acid gives a smaller weight loss than the substrate pretreated by distilled water.

When treated by nitric acid, the substrate is seriously corroded and its surface roughness is markedly increased,[34] which leads to a higher washcoat loading on the substrate, compared to the other two pretreating agents examined. As shown in Figure 4, the severe corrosion causes the formation of a loose layer on the substrate surface. This increases the severity of the flaws at the washcoat layer-substrate interface and, thus, increases the amount of adhesive failure. Moreover, the higher washcoat loading due to the pretreatment with nitric acid also leads to a larger amount of cohesive failure. It has been shown that the spallation-controlling crack for cohesive failure originates from the flaw within the washcoat layer.[13] The higher the washcoat loading, the larger

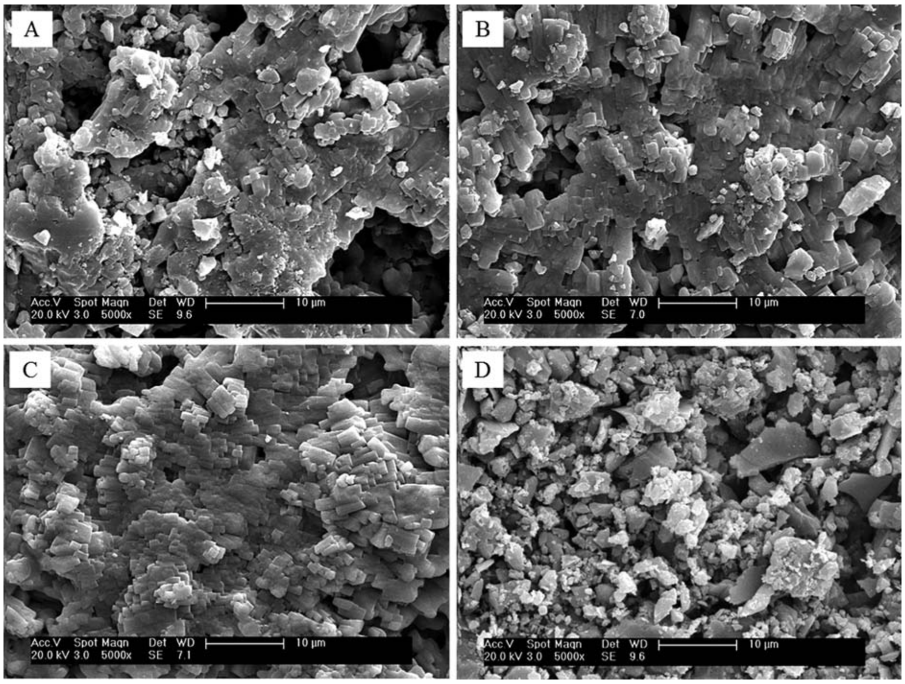

Figure 4. SEM micrographs of the monolith channel walls: (A) cordierite monolith without pretreatment, (B) water-pretreated monolith, (C) acetic acid-pretreated monolith, and (D) nitric acid-pretreated monolith.

the volume of washcoat layer, and thus, the higher the probability of cohesive failure will be. The cohesive failure of the washcoat layer is a stress-induced fatigue damage,[13] which depends on the stressed volume of a material because a larger volume increases the probability of existence of a critical flaw. Such a size effect on fatigue strength is a consequence of the statistical behavior of material fatigue.[37–39] Therefore, the substrate pretreated by nitric acid gives not only the highest washcoat loading but also the largest loss of weight.

Effect of the solid content

Three alumina sols with different solid contents (15, 20, and 25 wt %) were prepared and used to washcoat the monolithic substrates. Figure 5 shows the effects of the solid content on the washcoat loading and on the washcoat adhesion and cohesion. As expected, the loading of washcoat increases with the increase of the solid content. When the solid content amounts to 25 wt %, the loading of washcoat reaches its maximum value of 0.0612 g/monolith (11.3 wt %). However, as the solid content increases, the loss of weight increases at first, reaches its maximum value at the solid content of 20 wt %, and then decreases.

It can be deduced from the mechanical failure mechanism[13] that the adhesive and cohesive failures are both closely related to the solid content. With the increase of the solid content, the loading of washcoat gradually increases, and thus the amount of cohesive failure increases, arising from the aforementioned size effect on material fatigue. Conversely, a larger solid content results in a higher viscosity of alumina sol,[40–43] which can improve the adhesive bonding of the washcoat layer to the monolithic substrate. That is, the amount of adhesive failure will decrease with increasing the solid content. Thus, it can be seen that the adhesive and cohesive failures vary in opposite directions with the solid content.

As shown in Figure 5, when the solid content is increased from 15 to 20 wt %, the washcoat loading is almost doubled. Here, the effect of the solid content on the cohesive failure is likely to be more dominant than its effect on the adhesive failure, and thus, the loss of weight increases. However, as the solid content varies between 20 and 25 wt %, the increase in the washcoat loading is small, and the effect of the solid content on the adhesive failure is, therefore, more important, leading to a slight reduction in the weight loss.

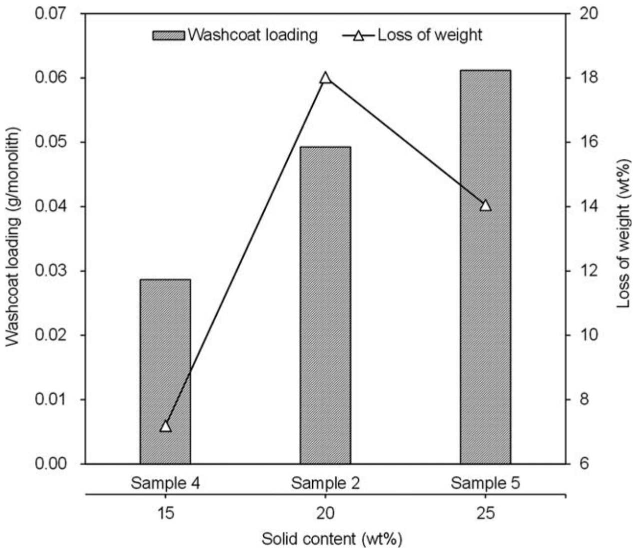

Figure 5. Influence of the solid content on the washcoat loading and on the washcoat adhesion and cohesion (Preparation conditions: pretreating agent of 50 wt % CH_3COOH, no additive, single washcoating).

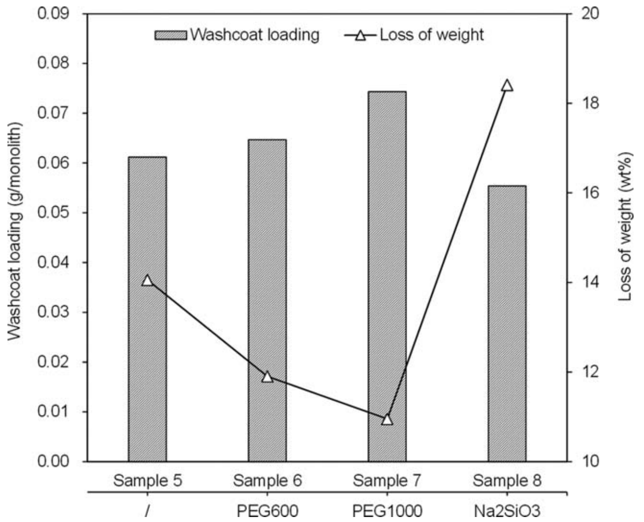

Figure 6. Influence of the additive on the washcoat loading and on the washcoat adhesion and cohesion (Preparation conditions: pretreating agent of 50 wt % CH_3COOH, solid content of 25 wt %, amount of additive of 3 wt %, single washcoating).

As well-known, the solid content of washcoating solutions/slurries is one of the key factors for preparing monolithic catalysts. A large solid content is usually required for a high-washcoat loading, provided only a single washcoating process is performed. Besides the washcoat adhesion and cohesion, there are many other properties of monolithic catalysts which are related to the solid content. For instance, a very large solid content will give an uneven washcoat layer,[41] that is, maldistribution of active material on the monolithic substrate. For colloidal solutions, a large solid content leads to a high viscosity and, thus, to an extremely poor stability of washcoating solutions due to their rapid gelation processes.[43] This study shows that when the solid content reaches 30 wt %, the rapid gelation results in a very poor flowability of alumina sol, and it is difficult for the sol to get into monolith channels. Therefore, an appropriate solid content is of great significance to the preparation of monolithic catalysts, and multiple washcoating process has to be used if a high-washcoat loading is desired.

Effect of the additive

In the preparation of washcoating solutions/slurries, various additives were often used by previous authors[12,20,22,26,44,45] to improve the quality of the washcoating solutions/slurries and/or to improve the textural/adhesive properties of the washcoat layers. In this work, polyethylene glycol 600 (PEG 600), polyethylene glycol 1000 (PEG 1000), and sodium silicate were selected as additives in alumina sol. The experimental results of the effects of the additive are shown in Figure 6. It is seen that sodium silicate leads to a little lower washcoat loading and a larger loss of weight, compared to the experimental results without additive. Nevertheless, the presence of PEG 600 or PEG 1000 not only increases the washcoat loading slightly but also reduces the loss of weight. In particular, PEG 1000 gives rise to the highest washcoat loading and the smallest loss of weight.

When a small amount of sodium silicate is added into alumina sol, its thermal decomposition products, for example, silica, will be doped within the washcoat layer and at the washcoat layer-substrate interface. The emergence of these distinct dopant flaws promotes both adhesive and cohesive failures, and the loss of weight, therefore, increases. After addition of PEG, the viscosity of alumina sol increases slightly, due to the formation of hydrogen bonds between the oxyethylene group of PEG and surface hydroxyl group of colloidal particles, improving the crosslinking of colloidal particles.[45] A higher viscosity of alumina sol leads to more difficulty in removing the excess liquid remaining in the channels after dipping, and thus to a little higher washcoat loading, although the solid content does not vary after addition of PEG. Furthermore, a higher viscosity of alumina sol improve the adhesive bonding of the washcoat layer to the monolithic substrate, as stated above. Therefore, the amount of adhesive failure will decrease after addition of PEG. However, the presence of PEG will generate new pores after calcination,[45] probably increasing the amount of cohesive failure slightly. As a consequence, the total decrease in the weight loss is not large due to the combined action of adhesive and cohesive failures. In addition, compared to PEG 600, PEG 1000 gives a higher viscosity of alumina sol,[45] and hence, results in a higher washcoat loading and a smaller loss of weight.

Effect of the amount of additive

Three alumina sols with different amounts of PEG 1000 (3, 6, 9 wt %) were prepared and used to examine the effects of the amount of additive on the washcoat loading and on the washcoat adhesion and cohesion. The experimental results are shown in Figure 7. It can be found that as the amount of additive increases the washcoat loading always increases slightly, and that the loss of weight decreases at first, reaches its minimum value at the additive amount of 6 wt %, and then increases with increasing the amount of additive.

The increasing viscosity of alumina sol with increasing the amount of additive leads to difficulty in removing the

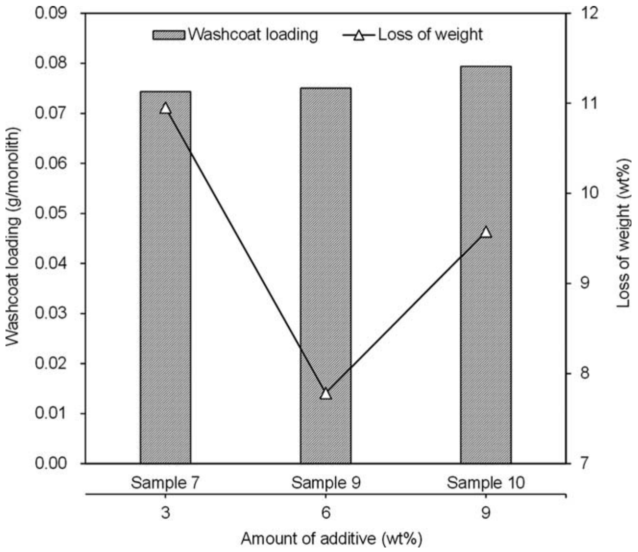

Figure 7. Influence of the amount of additive on the washcoat loading and on the washcoat adhesion and cohesion (Preparation conditions: pretreating agent of 50 wt % CH_3COOH, solid content of 25 wt %, additive of PEG 1000, single washcoating).

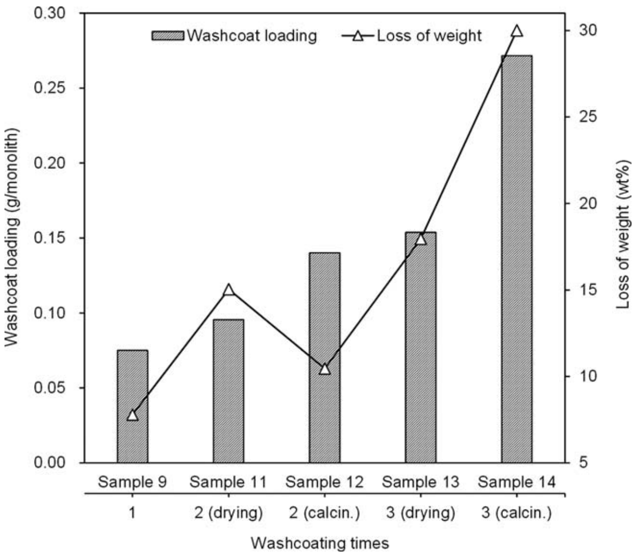

Figure 8. Influence of the washcoating times on the washcoat loading and on the washcoat adhesion and cohesion (Preparation conditions: pretreating agent of 50 wt % CH_3COOH, solid content of 25 wt %, additive of PEG 1000, amount of additive of 6 wt %).

excess liquid after dipping and, thus, to a slight increase in the washcoat loading. As stated above, the increasing viscosity of alumina sol also reduces the amount of adhesive failure, and thus reduces the loss of weight. Nevertheless, when the amount of additive is increased from 6 to 9 wt %, the loss of weight begins to rise. The reason for the increase is that after calcination the excess additive will generate a large number of new pores inside the washcoat layer,[45] which increases the severity of the flaws within the washcoat layer and, then, weakens the washcoat cohesion greatly. Moreover, the slight increase in the washcoat loading also leads to a small increase in the amount of cohesive failure. This might be another reason for the large weight loss of the monolithic catalyst prepared with a high amount of additive. Therefore, a moderate amount of additive is desired to improve the mechanical stability of monolithic catalysts.

Effect of the washcoating times

Figure 8 represents the effects of the washcoating times on the washcoat loading and on the washcoat adhesion and cohesion. It can be seen that with the increase of the number of washcoating times the washcoat loading increases, and that any multiple washcoating after calcination leads to a higher washcoat loading than the corresponding multiple washcoating after drying. Additionally, the loss of weight also increases with increasing the number of washcoating times. Among multiple washcoatings, the three-time washcoating after calcination leads to the largest loss of weight, followed by the three-time washcoating after drying. However, the two-time washcoating after calcination gives the smallest loss of weight, which is close to that of single washcoating.

The increasing loss of weight with the number of washcoating times is mainly ascribed to the increasing washcoat loading, resulting in the increase in the amount of cohesive failure. After calcination, an oxide layer is formed on the cordierite substrate, thus avoiding the redissolution of the washcoat layer when dipping is performed again, as may occur if the multiple washcoating after drying is used. A higher washcoat loading is, therefore, obtained for the multiple washcoating after calcination, compared to the multiple washcoating after drying. Meanwhile, it is also shown that the multiple washcoating after calcination will give a larger amount of cohesive failure, if only the aforementioned size effect on material fatigue is taken into consideration. Nevertheless, calcination not only improves the adhesive bonding of the washcoat layer to the cordierite substrate but also strengthens the cohesive strength of the washcoat layer. Thus, it is difficult to judge which of the multiple washcoatings after calcination and after drying will lead to a smaller loss of weight. From Figure 8, it can be seen that sample 12 has a slightly higher washcoat loading than sample 11, while the washcoat loading of sample 14 is much higher than that of sample 13. These reveal that the size effect on material fatigue is more important for the case of the three-time washcoating, but less important for the case of the two-time washcoating. Therefore, the two-time washcoating after calcination gives the smallest loss of weight while the three-time washcoating after calcination leads to the largest loss of weight.

It is shown that a single-factor-at-a-time method was used in this work for doing experiments to analyze the effects of the preparation process factors and that the catalyst samples with high-mechanical stabilities and satisfactory washcoat loadings, that is, sample 9 for single washcoating and sample 12 for multiple washcoating, have been obtained through the optimization of the factors. Nevertheless, the rough optimization method is unable to detect the presence of the interaction and combined effect of factors, and a precise optimization should be carried out by studying all the factors collectively by, for example, statistical experimental designs such as response surface methodology.[46] Furthermore, only one monolithic catalyst (γ-alumina-washcoated cordierite monolith) prepared by a dip-coating method was examined in this study. For other monolithic catalysts, different washcoating solutions/slurries, active materials, and/or preparation methods may be adopted. All of these factors will lead to the changes in the material properties and microstructures of the washcoat layer and its interface with the monolithic substrate, particularly the variation of the properties of various flaws, and hence, they strongly influence the mechanical stability of monolithic catalysts. If these factors have significant interactions with the process factors examined in this study, different effects of the preparation process factors on the mechanical stability will arise. Nevertheless, the scattering property of washcoat adhesion and cohesion exists, and the stress-induced fatigue damage nature are always true.[13] Therefore, similar optimization process can be performed and the previously proposed mechanical failure mechanism can be still used for the preparation factors analysis of the mechanical stability of monolithic catalysts. Finally, it should be mentioned that the optimization of a commercial monolithic catalyst is a multidimensional task. Besides the mechanical stability, many other catalyst properties such as catalytic activity should be optimized. The best values of all these desired properties may correspond to different optimal levels of the process factors; therefore, a compromise must be made among all these properties.

Conclusions

In this article, the factors affecting the mechanical stability of an alumina-washcoated cordierite monolithic catalyst during preparation were experimentally examined and, then, analyzed based on the mechanical failure mechanism previously proposed for cordierite monolithic catalysts. It is shown that the pretreating agent, solid content, additive, amount of additive, washcoating times all have great effects on the washcoat loading and on the washcoat adhesion and cohesion. Therefore, there is a great possibility of improving the mechanical stability of the monolithic catalyst through the optimization of the preparation process factors. The optimal preparation conditions obtained are the pretreating agent at 50 wt % acetic acid, the solid content at 25 wt %, the additive at PEG 1000, and the amount of additive at 6 wt %, resulting in a high-mechanical stability and a satisfactory washcoat loading. If multiple washcoating is performed for a high-washcoat loading, the two-time washcoating after calcination is recommended in this case as it gives a high-mechanical stability, close to that of single washcoating. It is also found that the loss of weight for monolithic catalyst mini-specimens with the same geometrical size and preparation history scatters in a large range, which is an intrinsic property inherited from the fatigue failure of active material. Additionally, the minor variation of the washcoat loading with specimen adds cause for the scatter of the weight loss for specimens. Finally, it has been confirmed that the previously proposed mechanical failure mechanism is an effective tool to factors analysis of the mechanical stability of monolithic catalysts.

Acknowledgment

Financial supports from the National Natural Science Foundation of China, under Grant Nos. 21176048 and 21376050, are gratefully acknowledged.

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Manuscript received Jan. 7, 2014, and revision received Mar. 26, 2014.