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Washcoating of γ-alumina on stainless steel microchannels

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ABSTRACT

In the present study, the effect of primer and slurry composition on the washcoat characteristics of γ-alumina on stainless steel substrate has been investigated. Washcoating was done following a two-step procedure: primer coating followed by slurry coating. Washcoat was characterized by SEM, adherence test and BET surface area measurement. For coating of the primer, Disperal with or without polyvinyl alcohol (PVA) was used. Without PVA, the sol settled in the microchannels whereas at high concentrations of PVA, the sol was too viscous. The optimum primer composition was found to be 2% Disperal and 4% PVA. In the subsequent slurry coating step, various properties of the slurry such as pH, viscosity, solid loading were optimized to obtain well-adhered, uniform washcoat on stainless steel substrate. PVA was added to the slurry to increase the binding and also enhance the viscosity, resulting in better adherence. An adverse effect of adding PVA was a reduction in the surface area. To reduce the amount of PVA and thereby its adverse effect, other binders (colloidal alumina and Disperal) were evaluated. Uniform well-adhered washcoats were obtained with particle size of γ-alumina less than 3 μm, and slurry composition: 14 wt.% γ-alumina, 2 wt.% PVA, 6 wt.% colloidal alumina and remaining water. Finally, the best washcoat obtained in this study was impregnated with 2% Rh–5% Ni and tested in the steam reforming of ethanol. For comparison, runs were also taken on powdered catalysts in a packed bed reactor at identical conditions and the conversions obtained in both the reactors were similar.

1. Introduction

Microchannel reactors are commonly used for conducting heterogeneous catalytic reactions. Success of such reactors depends on the formation of an adherent and uniform support layer on the microchannels. Even though the advantages of using microreactors have been reported for several reactions, the effect of slurry properties on the adherence, uniformity and loading of the washcoat layer has not been reported. These features depend on the slurry properties and more importantly on primer coating. The primer coating, consisting of a sol and/or viscosity modifier, is necessary to enhance the adherence of the alumina coating. Moreover, binders, viscosity modifiers and dispersants added in the slurry, can have a significant effect on the washcoat properties.

The washcoating of ceramic monoliths is well established, and different preparation methods can be found in reviews [1–3]. The slurry properties that are important for obtaining uniform and reproducible washcoats include: pH of the slurry, particle size, viscosity and slurry concentration [4–7]. In most of the studies, aluminum containing metallic substrates have been used in order to take advantage of the formation of an Al_2O_3 layer on the surface of the substrate on thermal treatment at high temperature [8–10]. For aluminum-free substrate, a primer coating can be used to form a thin layer of alumina which can enhance the adherence of the subsequent washcoat [11–13].

The stability of the slurry is important for obtaining uniform washcoats. To obtain a stable slurry, the particles in the slurry should be well-dispersed. This dispersion, in turn, depends on the net surface charge of the particles [14]. For alumina, it is well known that to obtain a stable suspension, the pH should be less than 5 or more than 9 [4,15]. Depending on the energetics of the adsorption process, some polymers, such as poly vinyl alcohol (PVA) can be used as binders whereas others such as poly (methacrylic acid) can be used as dispersants [14]. When PVA is used as a binder, then there can be a decrease in the surface area as well as the activity of the final catalyst [16]. Moreover, during calcination, large amount of gases can be formed, which may create cracks in the coating [14]. Instead of organic binders, inorganic binders such as, alumina sol or colloidal alumina, can be used as binders [1,17,18]. Germani et al. [16] reported washcoating of alumina on SS316 with different binders and found that the surface area decreased after addition of binders and this decrease depended on both the nature as well as concentration of binders.

In this study, the effect of slurry pH, slurry viscosity, various binders, primer and primer composition on washcoat characteristics such as morphology, uniformity, loading and coating

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Table 1
Composition and properties of slurries used for washcoating.

S. No.	Slurry composition[a]				Slurry properties		Washcoat properties	
	%, γ-Alumina	%, PVA	%, Disperal	%, CA[b]	pH	Viscosity[c], mPa s	Loading, mg/plate	Weight loss after 1 h sonication (%)
AS-1	10	0	0	0	3.5	3.01	17.1	11.0
AS-2	20	0	0	0	3.5	3.48	27.0	28.2
AS-3	30	0	0	0	3.5	4.5	38.8	47.8
AS-4	40	0	0	0	3.5	7.2	58.5	33.6
AS-5	20	4	0	0	2.0	91.1	25.6	10.0
AS-6	20	4	0	0	5.0	114.3	22.5	4.3
AS-7	20	4	0	0	6.5	188.4	na	na
AS-8	20	2	0	0	3.5	19.3	22.3	15.6
AS-9	20	3	0	0	3.5	47.8	22.0	12.8
AS-10	20	4	0	0	3.5	104.3	24.7	2.9
AS-11	14	1	6	0	3.5	97.1	23.3	1.5
AS-12	14	2	0	6	3.5	123.4	26.2	1.2

na = not analyzed.
[a] Remainder is water. The primer composition used with all these slurries was 2% Disperal + 4% PVA in water.
[b] CA = colloidal alumina.
[c] Viscosity at a shear rate of 200 s^{-1}.

thickness has been investigated. The substrate used was aluminum-free stainless steel (SS304).

2. Experimental

The steps involved in the washcoating of γ-alumina on the stainless steel substrates included fabrication of the microchannels, coating of the microchannels with primer, followed by washcoating with alumina slurry.

2.1. Fabrication of microchannels

Microchannels (depth: 400 μm; width: 500 μm; length: 20 mm; number of channels per plate: 25) were fabricated on SS304 plates by using a laser ablation unit (Model V3+, Laservall, Italy). Using this method, smooth and uniform channels were obtained. The channels were cleaned with a mixture of HCl and HNO_3, then with soap solution and finally sonicated in acetone for 30 min.

2.2. Primer coating

Primer deposition was done by using a mixture of boehmite sol and/or a binder in water. The boehmite sol was prepared by adding aluminum hydroxide powder (Disperal P2, average particle size = 45 μm, Sasol, Germany) to a 0.4 wt.% HNO_3 aqueous solution. The dispersion was stirred for 30 min and then aged for 2 days. During this period, the pH and viscosity gradually increased to a constant value, and did not change after that. When Disperal is dispersed in 0.4% HNO_3 aqueous solution, acid progressively breaks the powder particles. This process (peptization) is slow and requires about 48 h to reach equilibrium. This results in an increase in the pH and viscosity of the dispersion, as also reported by Valentini et al. [11]. Therefore, the boehmite sol was prepared two days before its use. The binder used was PVA and the concentration in the dispersion was varied from 0 to 4 wt.%. The boehmite sol was mixed with the required amount of PVA and stirred for 2 h before deposition on to the channels. The deposition was done following a five-step procedure: (i) filling of the microchannels with the primer dispersion, (ii) wiping off any excess dispersion from the area other than the microchannels of the plate, (iii) drying of the substrate at room temperature for 3 h and then at 120 °C for 8 h, (iv) scraping the primer deposited outside the channels, and (v) calcination at 600 °C for 5 h with a ramp rate of 2 °C min^{-1}. The primer composition was optimized based on the adherence of the washcoat deposited on the primer coating. For these runs, the composition of the slurry used for washcoating was kept the same (20 wt.% γ-alumina, 4 wt.% PVA, remainder water).

2.3. Slurry preparation and washcoating

After primer coating, the channels were coated with a slurry containing γ-alumina, PVA and in some cases, an alumina sol as

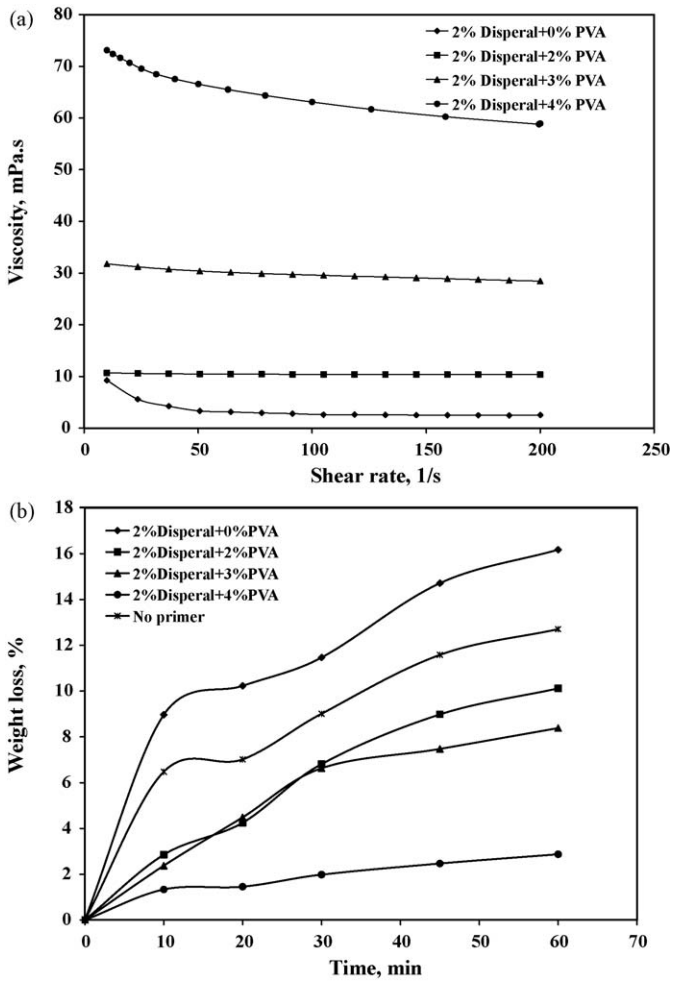

Fig. 1. Variation of viscosity with shear rate (a) and weight loss with sonication time (b) for different primer compositions.

binder. The binder used was Disperal or colloidal alumina (20 wt.% aluminum oxide in water; average particle size = 0.05 μm; Alfa Aesar, U.S.A.). The different slurry compositions used in this study are summarized in Table 1.

The average particle size of the as-received γ-alumina (Grace, U.S.A.) was 50 μm and this was reduced to less than 3 μm by wet milling in a ball mill (Pulverisette 6, Fritsch, Germany). For milling, a 30 wt.% aqueous slurry of alumina was prepared and the pH was adjusted to around 3 by adding concentrated nitric acid, to avoid gelation. The milled slurry was then mixed with the required amount of binder and the pH adjusted to the desired value by adding HNO_3 or KOH. After adding all the required components, the slurry was stirred for 2 h. Then, the slurry was deposited on to the channels by following the same five-step procedure, as used for primer coating (refer Section 2.2).

2.4. Characterization of primer, washcoating slurry and washcoat

The particle size distributions of the supplied and milled powders were measured by the laser beam scattering technique using a particle size analyzer (Malvern Mastersizer 2000, Malvern Instruments Ltd., U.K.). Viscosity of primers and alumina slurries with different compositions was measured by using a rheometer (AR-1000, TA Instruments, U.S.A.) in the shear rate range of 10–200 s^{-1}. The morphologies of primer coated and washcoated microchannels were observed by a scanning electron microscope (FEI Quanta 200, FEI, U.S.A.) operating at an accelerating voltage of 20 keV. The adherence of the washcoat was quantified by ultrasonication at 33 kHz. The samples were dipped in acetone and sonicated for 1 h. The samples were removed from the bath at 10 min intervals, dried and weighed. In each case, a small amount of slurry was dried and calcined at 600 °C for 5 h. The obtained powders were used to determine the BET surface area on a QuantaChrome unit (Autosorb-1C, Quantachrome, U.S.A.).

2.5. Activity test

The plates coated with γ-alumina using slurry AS-12 were employed in the steam reforming of ethanol on Rh–Ni/γ-Al_2O_3 catalyst. For this, a plate containing 25 microchannels (length of channels = 60 mm; depth = 400 μm; width = 500 μm) was used. 2% Rh and 5% Ni were co-impregnated on the γ-alumina by incipient wetness method using $RhCl_3 \cdot 3H_2O$ and $Ni(NO_3)_2 \cdot 6H_2O$. For comparison, runs were also taken on powdered catalysts (average particle size = 200 μm) in a packed bed reactor. Two types of powdered catalysts were used (i) γ-alumina impregnated with 2% Rh and 5% Ni (designated as PB1) and (ii) Rh and Ni impregnated on γ-alumina containing PVA (PB2). This support was made by drying slurry AS-12, followed by calcination at 600 °C and crushing the agglomerates to an average particle size of 200 μm. For all the runs, the molar ratio of water to ethanol was 6:1, and weight of catalyst/molar flow of ethanol was 2.23 g h mol^{-1}. The reactor temperature was varied from 500–600 °C.

3. Results and discussion

3.1. Effect of primer composition

The objective of primer coating is to form a thin layer of alumina in order to enhance the adherence of the subsequent washcoat. To study the effect of primer composition on adherence of the washcoat, different amounts of PVA (0–4 wt.%) were added to 2% Disperal in water. In each case, the pH of the primer suspension

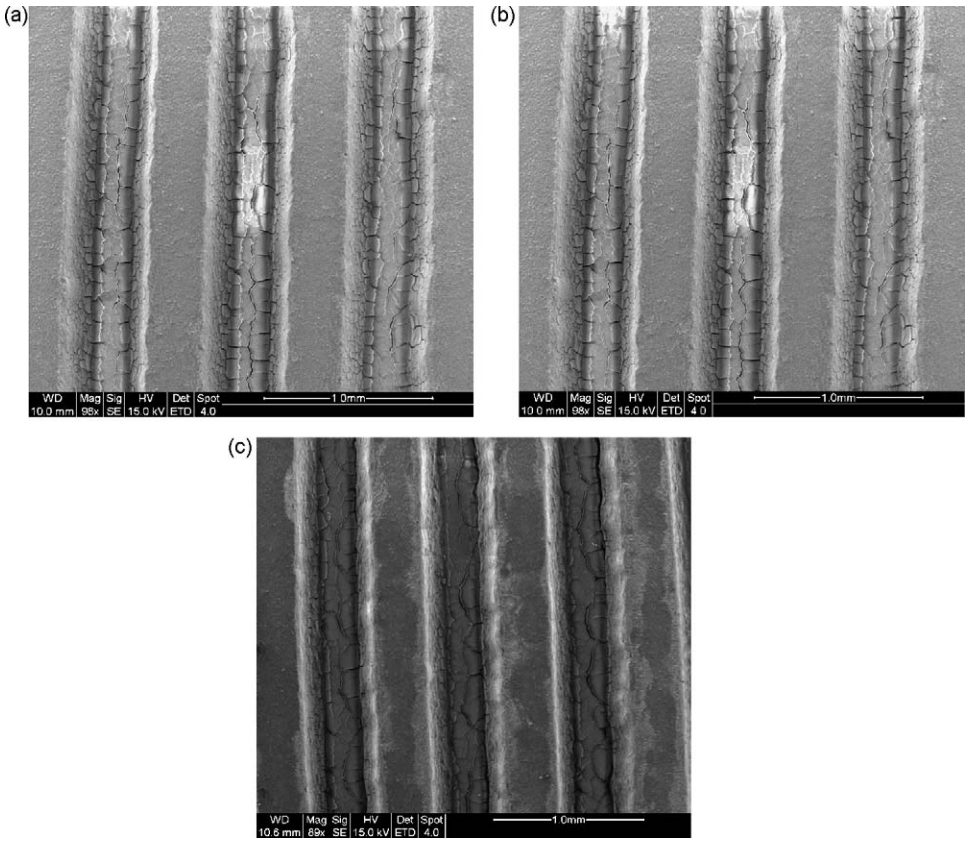

Fig. 2. SEM photographs for different slurry concentrations: (a) 10 wt.%, (b) 20 wt.%, (c) 30 wt.%.

was kept at 3.5. The viscosity of the suspension in which no PVA was added was very low but increased drastically with increasing wt.% of PVA (Fig. 1a). For a PVA concentration > 4 wt.%, the fluidity was very low, and handling of the dispersion was difficult. The increase in the weight of the substrate after the primer coating was approximately 2 mg. Assuming an apparent coating density of 1.5 g/cc, the calculated thickness of the primer coating was 2.3 μm. After the primer coating, all the samples were coated with an aqueous slurry containing 20 wt.% γ-alumina and 4 wt.% PVA. For comparison, this slurry was also coated on microchannels without any primer coating. Washcoat loading was obtained by taking the difference in weights of the microchannel plate before primer coating and after slurry washcoating. Within experimental error, there was no effect of primer composition on the final washcoat loading (∼24.7 mg/plate). The weight loss from the plate pre-coated with 2 wt.% Disperal and no PVA as primer was slightly higher than that from the plate washcoated without any primer pre-coating (refer Fig. 1b). This was most probably due to the settling of the primer in the channels, resulting in poor adherence of the subsequent coating. In contrast, with 2 wt.% Disperal + PVA the adherence was better and weight loss was lowest for (2 wt.% Disperal + 4 wt.% PVA) primer concentration. This primer composition was used in subsequent runs. In all cases, the weight loss increased with time of sonication till 45 min and leveled off thereafter.

3.2. Effect of slurry properties and composition

For this set of runs the primer composition was kept constant at 2% Disperal + 4% PVA in water.

3.2.1. Effect of slurry concentration (solids loading)

To study the effect of slurry concentration on washcoat adhesion and morphology, the solid content of the slurry was varied from 10 to 40 wt.%. For these runs, no binder was used. The variation of slurry viscosity with solid content is shown in Table 1 (S. No. AS-1–AS-4). For all the slurries, the variation of viscosity with shear rate was similar to that shown in Fig. 1a, and leveled off beyond a shear rate of 150 s^{-1}. Therefore, only the representative values at a shear rate of 200 s^{-1} are reported here. The slurry viscosity increased with solid loading. The change in viscosity was not significant between 10 to 30 wt.% solid loading but the viscosity increased by 60% as the solid loading was increased from 30 to 40 wt.%. This behavior is attributed to physical particle interactions, which are of three types [20]: (i) interparticle attraction (ii) hydrodynamic interactions (iii) particle–particle frictional interactions. At medium to high solid concentrations, the first and the third categories dominate over the second one, which increases the viscosity significantly. The SEM images of the coated channels are shown in Fig 2. It can be noticed that the coating was not appreciable on the channel walls and was highest at the

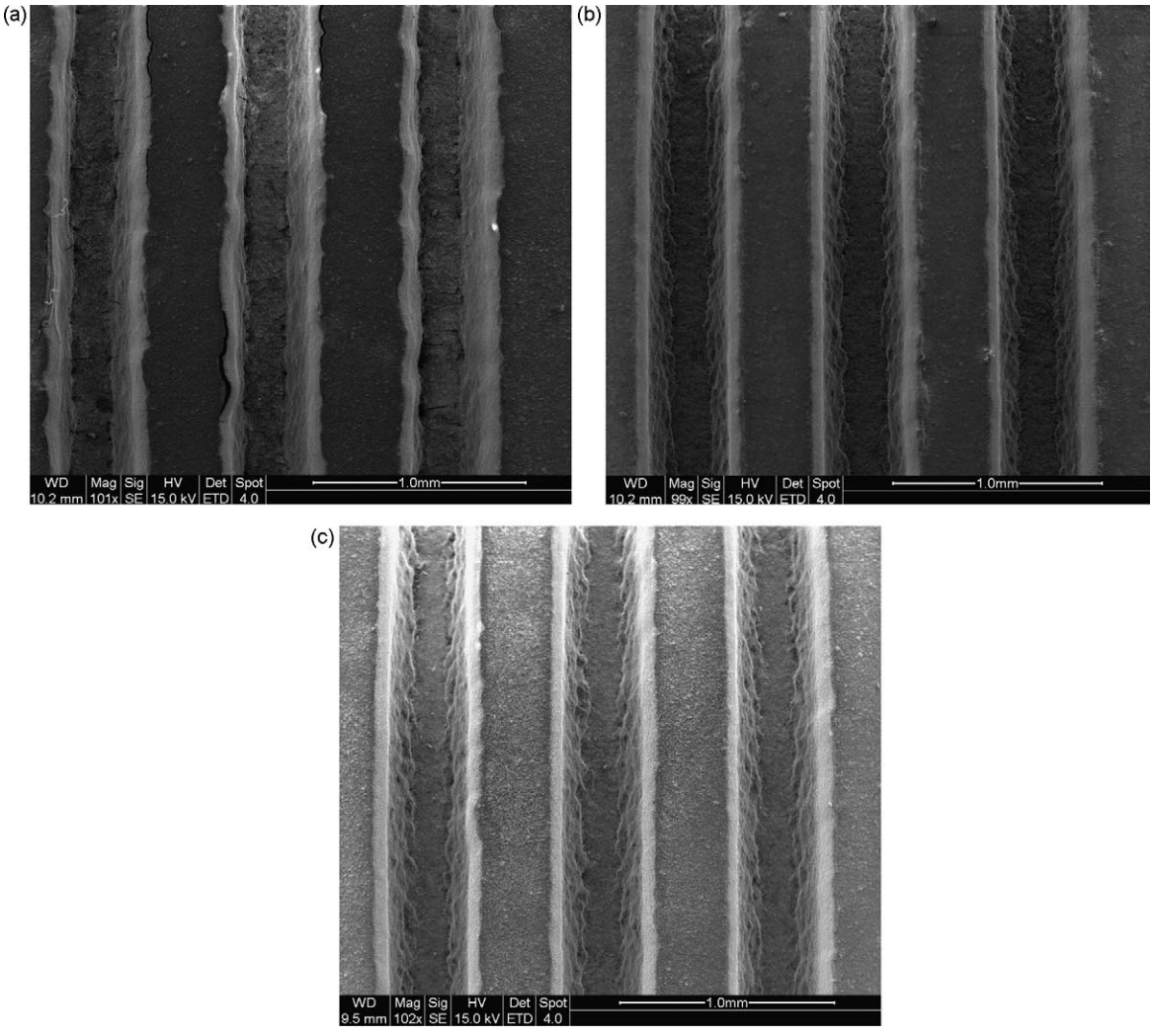

Fig. 3. SEM photographs of the washcoated microchannels for different PVA concentrations: (a) 2% PVA, (b) 3% PVA, (c) 4% PVA.

bottom. Moreover, for all the compositions, significant cracks can be seen. The washcoat loading and weight loss after 1 h of sonication for different solid loading are also given in Table 1. The loading increased approximately linearly with slurry concentration. The weight loss was significant for all the slurry coatings; it was highest for 30 wt.% slurry and lowest for 10 wt.% slurry. For all the slurries used, the weight loss was appreciable, and therefore, plates coated in this manner cannot be used for application in catalytic reactions.

3.2.2. Effect of pH

To study the effect of pH of the slurry on washcoat loading and adhesion, the pH of the slurry (20 wt.% γ-alumina + 4 wt.% PVA) was varied from 2 to 6.5 (refer S. No. AS-5–AS-7, AS-10; Table 1). The variation of slurry viscosity, washcoat loading and weight loss after sonication for 1 h with pH is given in Table 1. Slurry viscosity increased with pH. At low pH, the zeta potential is sufficiently large so that the alumina particles are well dispersed due to the strong electrostatic repulsive forces resulting in a high fluidity of the slurry. The increase in viscosity was highest between pH 5.0 and 6.5, which indicates that the dispersion of particles in the slurry was poor in this pH range [15,19]. Our results show that the pH only affects the adhesion and not the loading. In all cases, the washcoat loading was nearly the same (24 ± 1.6 mg). With increasing pH, the weight loss passed through minima at a pH of 3.5. At high pH, the dispersion of the slurry is poor, whereas at low pH there can be dissolution of smaller alumina particles resulting in poor adhesion. Therefore, a pH of 3.5 was used for further study.

3.2.3. Effect of PVA concentration

The effect of PVA concentration on adherence and morphology of washcoats was studied at a pH of 3.5 using 20 wt.% γ-alumina slurries with different PVA concentrations (0–4 wt.%). The results are given in Table 1. The slurry viscosity increased drastically with an increase in PVA concentration, and for PVA concentration beyond 4%, the fluidity decreased so much that the slurry could not be used for coating. In spite of the large change in slurry viscosity, the washcoat loading was nearly the same (24.5 ± 2.5 mg). This is in contrast with some studies on washcoating of monoliths with slurries of different viscosities [4,7], where the loading found to increase with an increase in viscosity. The reason for this observation is that the total weight of the slurry put in the channels as well as the solid loading was the same. Therefore, the weight gain after coating with slurries of different viscosities but same solids loading should be equal. In contrast, as PVA concentration increased, the weight loss decreased drastically and was about 3% after 1 h sonication for slurry containing 4 wt.% PVA. The SEM images (Fig. 3) show that the cracks in the washcoat decreased with an increase in the concentration of PVA. Shrinkage and gas formation during calcination may be responsible for the formation of cracks. The approximate thickness of the coating on the sidewalls of the microchannels was measured from these photographs and was found to be maximum for 4% PVA (~65 μm) and almost negligible for coating with the slurry without any added PVA (refer Fig. 2), even though the washcoat loading was similar in both the cases. When the viscosity of the slurry is low, the washcoat is not distributed uniformly over the surface of the channel and the amount of washcoat deposited is low on the walls and more at the bottom. These results are in agreement with those presented by Germani et al. [16], who reported that viscosity affects the form of the final washcoat. The surface area of the dried and calcined powder obtained from 20% γ-alumina + 4% PVA slurry(161 $m^2 g^{-1}$) was relatively lower when compared to that of γ-alumina powder (183 $m^2 g^{-1}$).

3.2.4. Effect of binder

By using 4 wt.% PVA as binder, the surface area of the washcoat decreased. Therefore, the possibility of using other binders was tried. Two inorganic binders, viz. Disperal and colloidal alumina, along with small amounts of PVA to adjust the viscosity, were tested (AS-11 and AS-12; Table 1). The viscosity, pH and solids content were approximately the same as that of AS-10 (refer Table 1) with which best results were obtained. Though γ-alumina content is lower (14 wt.%) in samples AS-11 and AS-12 when compared to that of AS-10 (20 wt.%), the total γ-alumina obtained with all the three samples after calcination was approximately the same, because after calcination boehmite is converted to γ-alumina. For both the suspensions prepared using inorganic binders, the degree of shear thinning was very high at lower shear rates and the viscosity was almost equal to that of AS-10 slurry at higher shear rates (Fig. 4a). The washcoat loading obtained with different binders is also given in Table 1. There was no significant effect of binder on the washcoat loading and for all the three slurries, the loading was 24.7 ± 1.5 mg. The lowest weight loss was obtained when colloidal alumina was used as the binder (Fig. 4b). As shown in the SEM photographs of Fig. 5, when colloidal alumina was used as the binder, the washcoat did not have any cracks; whereas large cracks were formed with Disperal as binder. This may be attributed to the significant shrinkage of Disperal during calcination. Small holes can be seen in the SEM image of the coating made with AS-10. These holes are most likely due to the formation of large amount of gas during calcination. Because of the particle size difference between Dispersal and colloidal alumina, the binding was more effective in the case of colloidal alumina. During evaporation, initially large particles come closer to each other. As evaporation continues, the small binder particles come into the gaps between the larger particles, due to

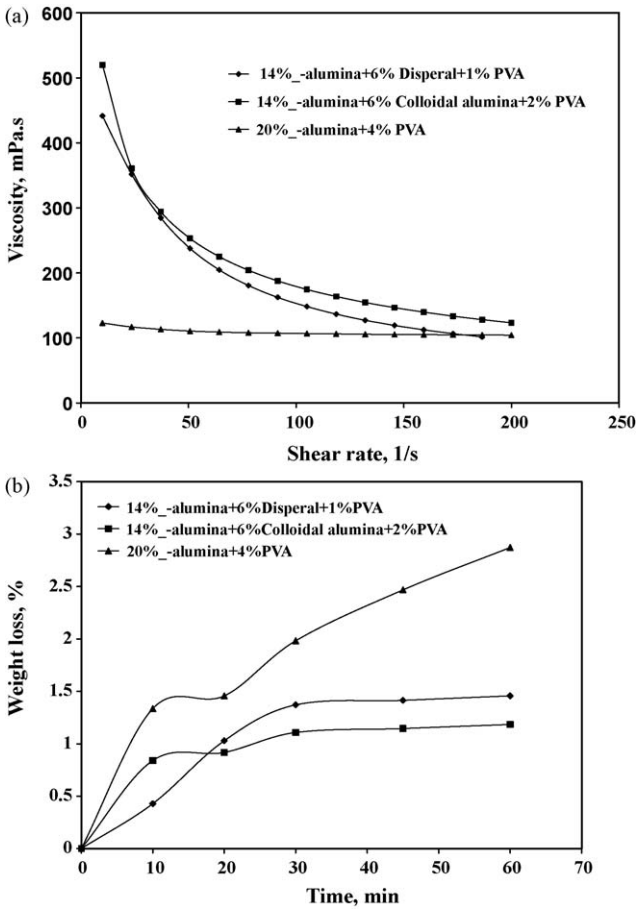

Fig. 4. Variation of viscosity with shear rate (a) and weight loss with sonication time (b) for different binders.

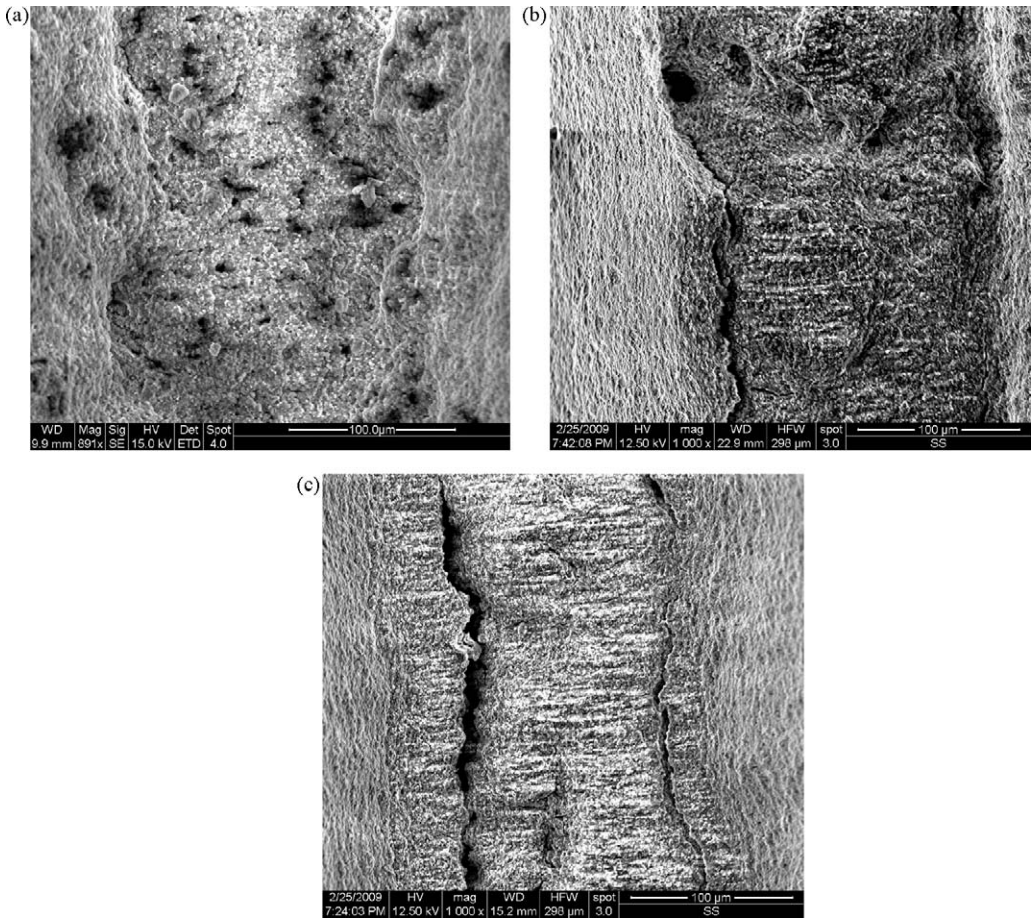

Fig. 5. SEM micrographs after coating with slurry of different binders: (a) 4 wt.% PVA, (b) 6 wt.% colloidal alumina + 2 wt.% PVA, (c) 6 wt.% Disperal + 1 wt.% PVA.

capillary forces [1]. For comparison, the slurry with Disperal as binder was coated without any primer pre-coating and it was found that the weight loss was higher (~4.4%) than that obtained with primer pre-coat (~1.5%). Therefore, primer is essential for obtaining well-adhered washcoats. The surface area of dried and calcined powder obtained with slurry containing colloidal alumina as binder (173 $m^2\ g^{-1}$) was higher than that obtained with slurry containing only PVA (161 $m^2\ g^{-1}$) as binder; however it was lower than that of fresh γ-alumina (183 $m^2\ g^{-1}$).

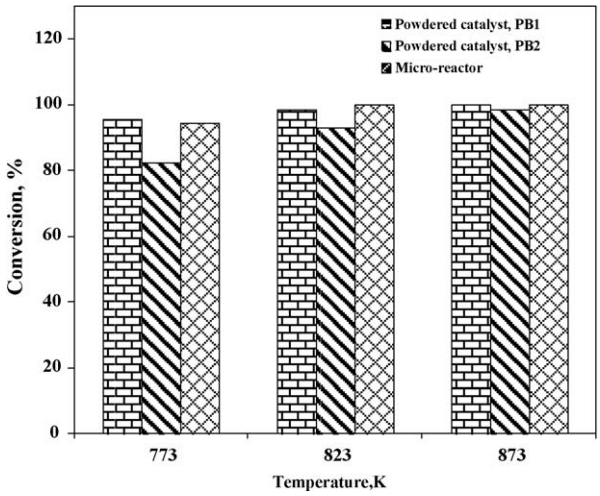

Fig. 6. Conversion of ethanol obtained in packed bed and microreactors with different catalysts.

3.2.5. Activity test

The conversion of ethanol obtained in the microreactor and in the packed bed reactor with the two different powder catalysts (PB1 and PB2) at different temperatures is shown in Fig. 6. As can be seen from Fig. 6, the presence of PVA in the support marginally reduced the conversion in the packed bed reactor. For example, at a temperature of 823 K, the conversion of ethanol with catalyst PB2 was 92.9% whereas with catalyst PB1, it was 98.5%. The conversion obtained in the microreactor was higher than that obtained in a packed bed reactor with the catalyst containing PVA (PB2). A possible reason for this could be the longer diffusional path in the powdered catalyst (average size = 200 μm) compared to the washcoat thickness of approximately 65 μm in the microchannels.

4. Conclusions

From the results obtained, it can be concluded that the primer coating is essential for obtaining uniform, adherent washcoats on the stainless steel microchannels. Optimum primer composition obtained in this study was 2% Disperal + 4% PVA in water. For obtaining uniform and well-adhered washcoats, the pH of the slurry should be around 3.5 and the slurry viscosity in the range of 90–120 mPa s at a shear rate of 200 s^{-1}. Addition of colloidal alumina as a binder reduces the cracks in the washcoat and improves the washcoat adherence. The plates washcoated with the optimum slurry composition and impregnated with 2%Rh–5%Ni performed satisfactorily in the steam reforming of ethanol.

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