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# Single step direct coating of 3-way catalysts on cordierite monolith by solution combustion method: High catalytic activity of $Ce_{0.98}Pd_{0.02}O_{2-\delta}$

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A new process of coating of active exhaust catalyst over $\gamma$-$Al_2O_3$ coated cordierite honeycomb is reported here. The process consists of (a) growing $\gamma$-$Al_2O_3$ on cordierite by solution combustion of $Al(NO_3)_3$ and oxylyldihydrazide (ODH) at 600 °C and active catalyst phase $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ on $\gamma$-$Al_2O_3$ coated cordierite again by combustion of ceric ammonium nitrate and ODH with $1.2\times 10^{-3}$ M $PdCl_2$ solution at 500 °C. Weight of active catalyst can be varied from 0.02 to 2 wt% which is sufficient but can be loaded even up to 12 wt% by repeating dip dry combustion. Adhesion of catalyst to cordierite surface is via oxide growth which is very strong. About 100% conversion of CO is achieved below 80 °C at a space velocity of 880 $h^{-1}$. At much higher space velocity of 21,000 $h^{-1}$, 100% conversion is obtained below 245 °C. Activation energy for CO oxidation is 8.4 kcal/mol. At a space velocity of 880 $h^{-1}$ 100% NO conversion is attained below 185 °C and 100% conversion of 'HC' ($C_2H_2$) below 220 °C. At same space velocity 3-way catalytic performance over $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ coated monolith shows 100% conversion of all the pollutants below 220 °C with 15% of excess oxygen. In this method, handling of nano material – powder is avoided.

**KEY WORDS:** monolith; cordierite; honeycomb; active phase; 3-way catalyst.

## 1. Introduction

Automobile exhaust contains significant amount of unburned hydrocarbons (~500 ppm) together with up to 10,000 ppm of CO and ~1000 ppm of NO. Removal of these pollutants requires a single formulated catalyst. Such a catalyst is termed as the three-way catalyst (TWC). By early 1980s all the constituents necessary for the operation of TWC were in place and their use became wide spread. For automobile applications such a TWC is to be coated or loaded on a ceramic monolith support having wall structure like honeycomb. Monolith is first coated with high surface area oxides like $\gamma$-$Al_2O_3$ and the process is called washcoating. After washcoating, the three-way catalyst, usually called active phase is coated over the monolith. Numerous methods exist for washcoating and active phase coating. Most of them have been reviewed by Nijhuis *et al.* [1]. Usually sol–gel is employed for washcoating [2] and slurry coating for the active catalyst phase [3].

Ceria has been widely employed in three-way automobile catalyst mainly due to its oxygen storage capacity that allows effective catalyst operation under conditions with oscillating oxygen concentration [4–7]. Besides the oxygen storage capacity (OSC), ceria exhibits strong metal support interaction with precious metals such as Pt, Pd or Rh enhancing their catalytic activity. In the last few years, the use of palladium (Pd) has gained renewed attention. Pd is preferred because, Pd based catalysts seem to be more suitable to meet the stringent emission regulations and also it is the cheapest precious metal [8–10].

One way to increase the catalytic activity is to disperse Pt, Pd, Cu, Ag and Au in ionic form by making nano crystalline $Ce_{1-x}M_xO_{2-\delta}$ ($M = Cu^{2+}, Pd^{2+}, Pt^{2+}, Ag^{+1}, Au^{3+}$) employing the solution combustion method [11–16]. Since $CeO_2$ is a reducible oxide, under highly oxidizing environmental condition Pt, Pd, etc. can remain in oxidized state. Loading of active phase over cordierite monolith using slurry does not lead to good adhesion. Addition of binder and surfactant is also needed. It is therefore desirable to grow active phase directly on the monolith surface without going through making of catalyst powder and binder. Here we extended the method to prepare the active phase $Ce_{1-x}M_xO_{2-\delta}$ ($Pd^{2+}$) nano crystalline powder by solution combustion method to grow the active phase on cordierite honeycomb substrate directly. Among various advantages in this method, washcoat and active phase loading required is about 2–3% by wt. of honeycomb and the total precious metal loading is 20% of what is generally employed [17,18]. Hence the process is economical. Adhesion is strong due to *in situ* growth of nano-crystalline oxides over the cordierite honeycomb support. Here we report our studies of monoliths coated with high surface area $\gamma$-$Al_2O_3$ as washcoat and $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ as the active catalyst phase. Catalyst itself is new in its making as the metal present is in the

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ionic state (Pd in +2 state) instead of Pd in metallic state. Performance of the honeycomb catalyst has been examined by performing 3-way catalytic reactions.

## 2. Experimental

$\gamma$-$Al_2O_3$ can be made by heating the stoichiometric amount of $Al(NO_3)_3$ and oxylyldihydrazide, $(CONHNH_2)_2$ (ODH).

$$2Al(NO_3)_3 + 3(CONHNH_2)_2 \longrightarrow \gamma\text{-}Al_2O_3 + 6CO_2 + 9N_2 + 9H_2O.$$

Similarly, $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ can be prepared as follows [12]:

$$\begin{aligned}&10(1-x)(NH_4)_2Ce(NO_3)\\&+24(1\text{-}x)(CONHNH_2)_2 + 10\times PdCl_2 \longrightarrow\\&10Ce_{1-x}Pd_xO_{2-\delta} + 88(1\text{-}x)N_2 + 48(1\text{-}x)CO_2 +\\&(102-112x)H_2O + 20xHCl\end{aligned}$$

The solution containing ceric ammonium nitrate, ODH and $PdCl_2$ is rapidly heated at 500 °C to form nano crystalline $Ce_{1-x}Pd_xO_{2-\delta}$ . In a typical preparation of $\gamma$-$Al_2O_3$ , 0.09 M $Al(NO_3)_3$ and 0.133 M oxylyldihydrazide (ODH) are dissolved in $H_2O$ followed by the combustion at 600 °C and combustion of 0.06 M ceric ammonium nitrate and 0.144 M ODH with $1.2\times10^{-3}$ M $PdCl_2$ solution at 500 °C gives $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ . Instead of making powder catalyst as mentioned above, honeycomb is dipped into the solution and rapidly heated at 600 °C for $\gamma$-$Al_2O_3$ and 500 °C for $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ . Combustion occurs on the wet surface of cordierite monolith dipped in the precursor solution yielding the fine particle growth of washcoat/active phase over the oxide support directly. Since the material is coated in the form of a thin film on cordierite surface, time required for the growth of $\gamma$-$Al_2O_3$ or $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ is small. Generally, 3–5 min is sufficient for the coating of each layer. Process is repeated until we get the desired amount of coating. Since the oxide formed is not soluble in the solution, repeated growth of oxide is achieved. No binder is required for the active phase coating. Monolithic supports, which have been used for this study, are of 2.5 cm in length, 1.876 cm in diameter with cell density of 400 cells/in$^2$ made by BHEL, Bangalore. Washcoat loading is 36.2 g/L and metal loading is 0.45 g/L

$Pd_{0.02}Ce_{0.98}O_{2-\delta}$ coated honeycomb was characterized by X-ray powder diffraction, X-ray photoelectron spectroscopy and Scanning electron microscopy.

Catalytic studies were carried out using a fully computer controlled temperature programmed reaction system fabricated here in the laboratory equipped with a quadrupole mass spectrometer SX200 (VG Scientific Ltd., England) and an online gas chromatograph (Mayura Analytical Pvt. Ltd., Bangalore). Two cylindrical pieces of coated honeycomb are taken in a quartz tube inside a tubular furnace. Gases were from M/S Bhuruka Gases Ltd. (India) with 5.14 vol% CO in He, 4.74 vol% NO in He, 5.48 vol% $C_2H_2$ in He, 99.98% pure $O_2$ and 99.9 % pure He for balance in the present study.

Catalytic experiments were carried out at atmospheric pressure in the temperature range of 40–400 °C. The gas flow rate was 100 cc/min. which gives rise to a space velocity of 880 h$^{-1}$ (taking 0.5 void fraction). There was no preheating of the gases. The total amount of $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ catalyst loaded was equal to 125 mg/monolith. Heating rate was 5 °/min. Kinetic studies for CO oxidation are carried out at a constant flow of 600 cc/min with half piece of monolith and at different residence times (by changing the length of the monolith). With this we get the space velocities, 21,083, 10,540, 5,270 and 2,635 h$^{-1}$ (residence times are 0.17, 0.34, 0.68, 0.85 s.)

## 3. Results and discussion

In figure 1(a–c) SEM of bare monolith, monolith coated with $\gamma$-$Al_2O_3$ and monolith with $\gamma$-$Al_2O_3$ + active catalyst phase are shown respectively. In figure 1(a) we see the plate like morphology while in figure 1(b) we see the white porous material over the surface. Figure 1(c) shows the $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ surface on cordierite. Difference in the surface morphology is apparent. Elemental analysis was done by EDAX. Crossection of cordierite surface gives 90% of aluminum after alumina coating. Clearly Al concentration increases upon coating of $\gamma$-$Al_2O_3$ . Crossectional view of $\gamma$-$Al_2O_3$ /cordierite is shown in figure 1(d). Thickness of $\gamma$-$Al_2O_3$ is estimated to be 250–300 nm. Chemical analysis of the top surface after active phase coating gave the ratio 0.94:0.04 of Ce to Pd which is close to the composition taken in the preparation. There is no weight loss of the material after sonication for over one hour showing adhesion of $\gamma$-$Al_2O_3$ and $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ to the cordierite surface is very strong. The photograph of coated and uncoated monolith is shown in figure 2.

X-ray diffraction pattern of bare cordierite surface is given in figure 3(a). The powder pattern was Rietveld refined with Rp = 17.56% and Wrp = 22.87 using GSAS and this pattern is fitted to orthorhombic structure with Cccm space group. The lattice parameters are $a$ = 16.99 Å, $b$ = 9.88 Å and $c$ = 9.39 Å. Accordingly indexed pattern of cordierite surface is given in figure 3(a). XRD pattern of $Al_2O_3$ coated cordierite is shown in figure 3(b). Since the coating is thin, lines due to $\gamma$-$Al_2O_3$ are not discernable. XRD of active phase $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ grown over $\gamma$-$Al_2O_3$ /cordierite surface is given in figure 3(c). In addition to lines due to cordierite, $CeO_2$

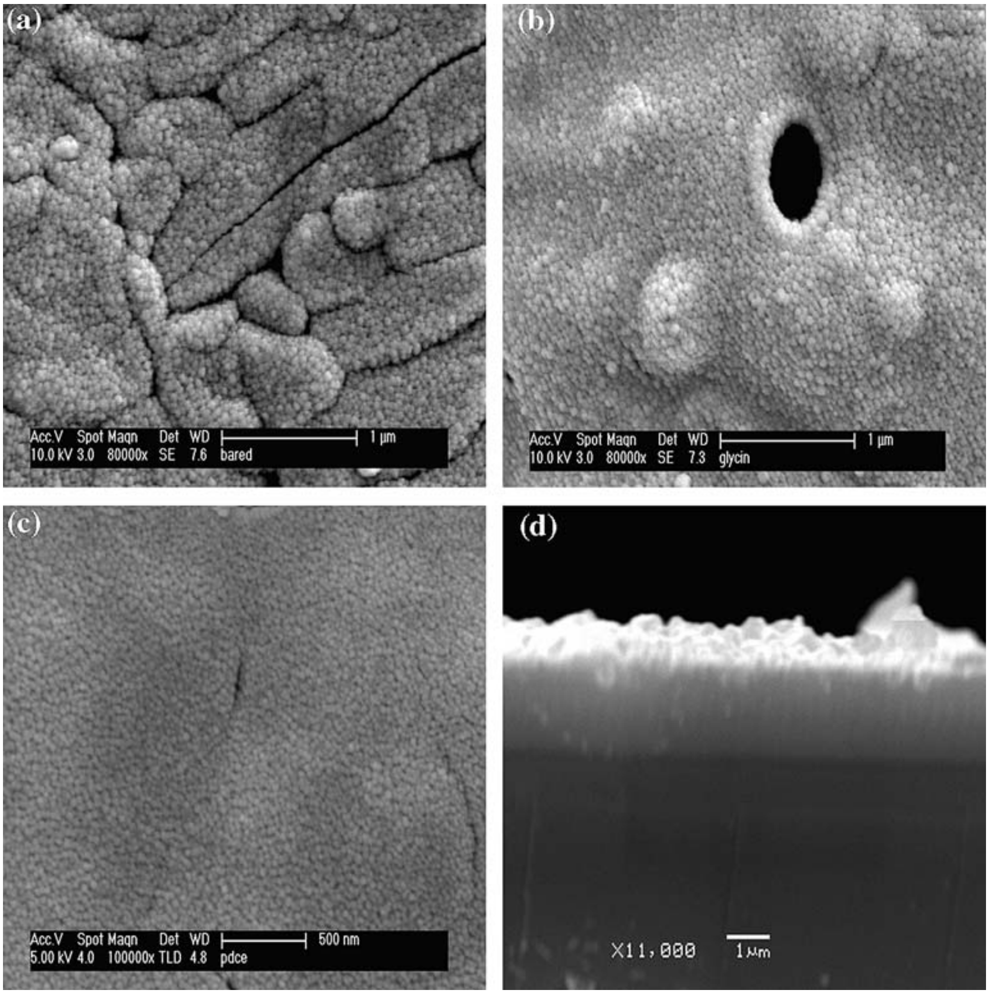

Figure 1. SEM images of (a) bare cordierite surface, (b) cordierite surface coated with $\gamma$-$Al_2O_3$ , (c) cordierite surface coated with $\gamma$-$Al_2O_3$ followed by $Ce_{1-x}Pd_xO_{2-\delta}$ and (d) crossectional view of cordierite surface coated with $\gamma$-$Al_2O_3$.

diffraction lines in fluorite structure are observed demonstrating the growth of polycrystalline $CeO_2$ over the cordierite surface. XRD of $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ powder by combusting the same solution used for dip dry combustion is given in figure 3(d) for comparison. The diffraction lines of $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ powder (figure 3(d)), does not show any peak due to Pd metal or PdO [12]. From the half width, crystallites size of the $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ powder is 30–40 nm. Diffraction lines of $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ on the monolith are broad indicating crystallites on the monolith are much smaller than the crystallite of $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ powder.

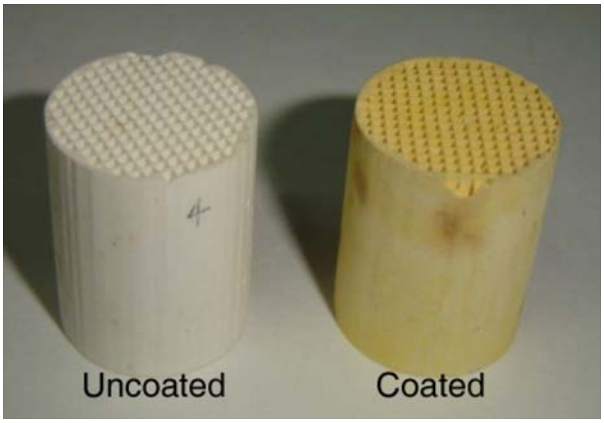

Figure 2. Photograph of coated and uncoated honeycomb.

Adhesion of $\gamma$-$Al_2O_3$ and $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ is due to oxide growth on cordierite. Growth of $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ on the cordierite can be rationalized as follows: d(404) or d(440) of cordierite is ~2.0 Å which is close to (400) of $\gamma$-$Al_2O_3$ . So, growth of $\gamma$-$Al_2O_3$ in [100] direction over cordierite is possible. Lattice parameter of $CeO_2$ is 5.41 Å and cubic ceria can grow over $\gamma$-$Al_2O_3$ in [100] direction with a basal plane rotated by 45 ° because sqrt(2) $\times$ 5.41 = 7.65 Å which is close to 'a' of $\gamma$-$Al_2O_3$ 8.01 Å . Therefore, growth of $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ is possible over cordierite with $\gamma$-$Al_2O_3$ as an interface. Chemically, cordierite is $Mg_2Al_4Si_5O_{18}$ and the bonding is mostly covalent. On this surface, covalent $Al_2O_3$ can

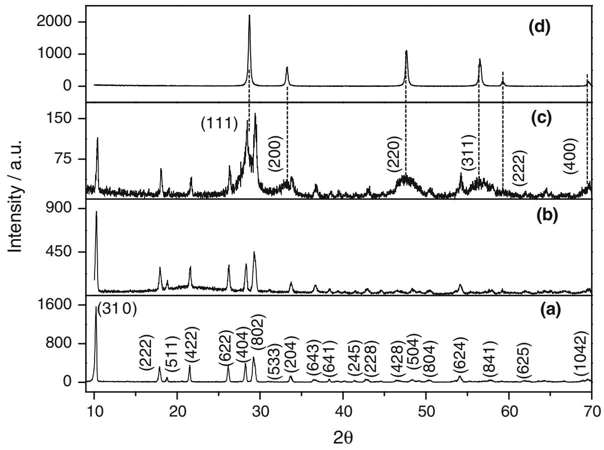

Figure 3. XRD pattern of (a) bare cordierite surface; (b) cordierite surface coated with $Al_2O_3$ ; (c) $Ce_{1-x}Pd_xO_{2-\delta}$ powder and (d) cordierite surface coated with Al2O3 followed by $Ce_{1-x}Pd_xO_{2-\delta}$.

grow easily. Epitaxial growth of $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ over $(1\bar{1}02)\,Al_2O_3$ has been done by pulsed laser deposition [19]. $CeO_2$ can be grown over $(1\bar{1}02)Al_2O_3$ and over that $YBa_2Cu_3O_7$ can be grown epitaxially [20]. Growth of $YBa_2Cu_3O_7$ on single crystal surface of $\alpha$-$Al_2O_3$ $(1\bar{1}\ 02)$, $SrTiO_3(100)$ is well known. Thus, following the idea of epitaxial growth on oxide, we have grown polycrystalline $\gamma$-$Al_2O_3$ on cordierite and $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ over $\gamma$-$Al_2O_3$ coated cordierite by solution combustion method. This way handling of nano $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ is completely avoided. Due to the direct growth oxide on the oxide support, adhesion of the active phase is very strong.

Figure 4(a) shows the XPS of Pd(3d) core levels recorded from the surface of $Ce_{0.99}Pd_{0.01}O_{2-\delta}$ coated honeycomb. $Pd(3d_{5/2,3/2})$ peaks for Pd metal powder and $Pd^{+2}$ ion in $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ powder are also given for comparison. Binding energy of $Pd(3d_{5/2})$ in $CeO_2$ matrix is observed at 337.5 eV. $Pd(_{5/2})$ peaks in Pd metal and $Pd^{2+}$in PdO are observed respectively at 335.1 and 336.8 eV. $Pd(3d_{5/2})$ peak is observed at 337.5 in the coated material. Therefore, the oxidation state of palladium is $+2$ state in the active phase. Ce is in $+4$ state as can be seen for the Ce(3d) spectrum with characteristic satellites (figure 4(b)). XPS of $Ce^{+4}(3d)$ in $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ powder and $CeO_2$ are also shown for comparison.

CO oxidation over the monolith catalysts is carried out with 10,000 ppm of both CO and $O_2$. Heating rate was kept constant at 5°C/min. Figure 5(a) shows the CO oxidation by $O_2$. About 100% CO conversion occurs below 100 °C. We have examined the performance at a higher gas flow rate of 600 cc/min. About 100% CO conversion occurs below 245 °C. Performance of the monolith at different space velocities for CO oxidation is shown in figure5(b). CO oxidation with concentration of CO and $O_2$ 2000 ppm each, at different residence times (by changing the length of the monolith) and keeping the flow rate constant at 600 cc/min is shown in figure 5(c). From the percent conversion versus V/F (V, volume of the monolith), actual rates of the CO conversion in moles $m^{-3}$ $s^{-1}$ were obtained. In figure 5(d), the ln(rate) vs. 1/T is given, which gives an activation energy of 8.4 kcal/mol. Activation energy is indeed low. If we compare the rates of CO oxidation between monolithic catalyst and powder catalyst, we find approximately 4 times increase in the rate at the same temperature when $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ is grown on cordierite surface. This is to be expected because, crystallites size over monolithic surface is much smaller than powder as seen from XRD study, leading to high surface area and dispersion.

A Comparison with the literature for CO oxidation reaction over monolithic summarized in table 1. Tagliferri *et al.* [16] have studied three way catalytic properties of different catalysts. Arnby *et al.* [21] have studied the effect of the platinum dispersion over the washcoat. Although their catalyst has less metal loading, they have taken very less CO concentration along with very high oxygen concentration. With $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ rate of CO oxidation is 0.2 moles $m^{-3}$ $s^{-1}$ at 200 °C.

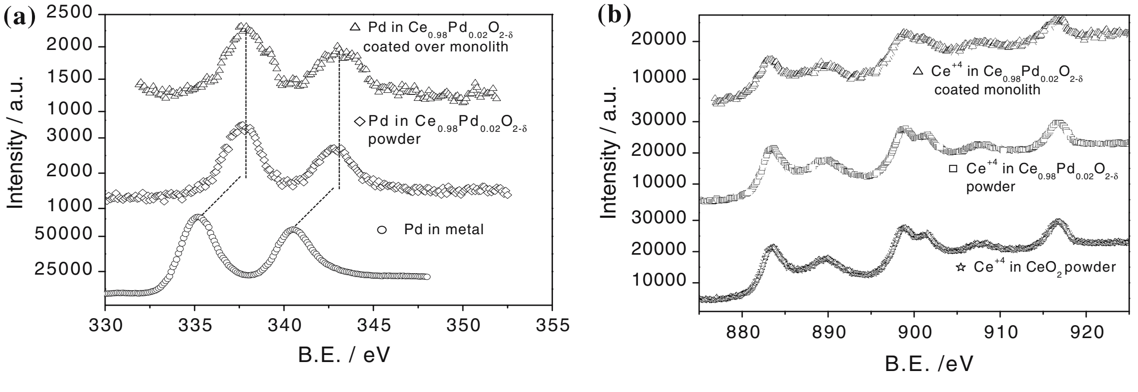

Figure 4. XPS of (a) Pd(3d) core levels from Pd metal, $Ce_{1-x}Pd_xO_{2-\delta}$ powder and $Ce_{1-x}Pd_xO_{2-\delta}$ coated cordierite surface and (b) Ce (3d) core level regions of $CeO_2$, $Ce_{1-x}Pd_xO_{2-\delta}$ powder and $Ce_{1-x}Pd_xO_{2-\delta}$ coated cordierite surface.

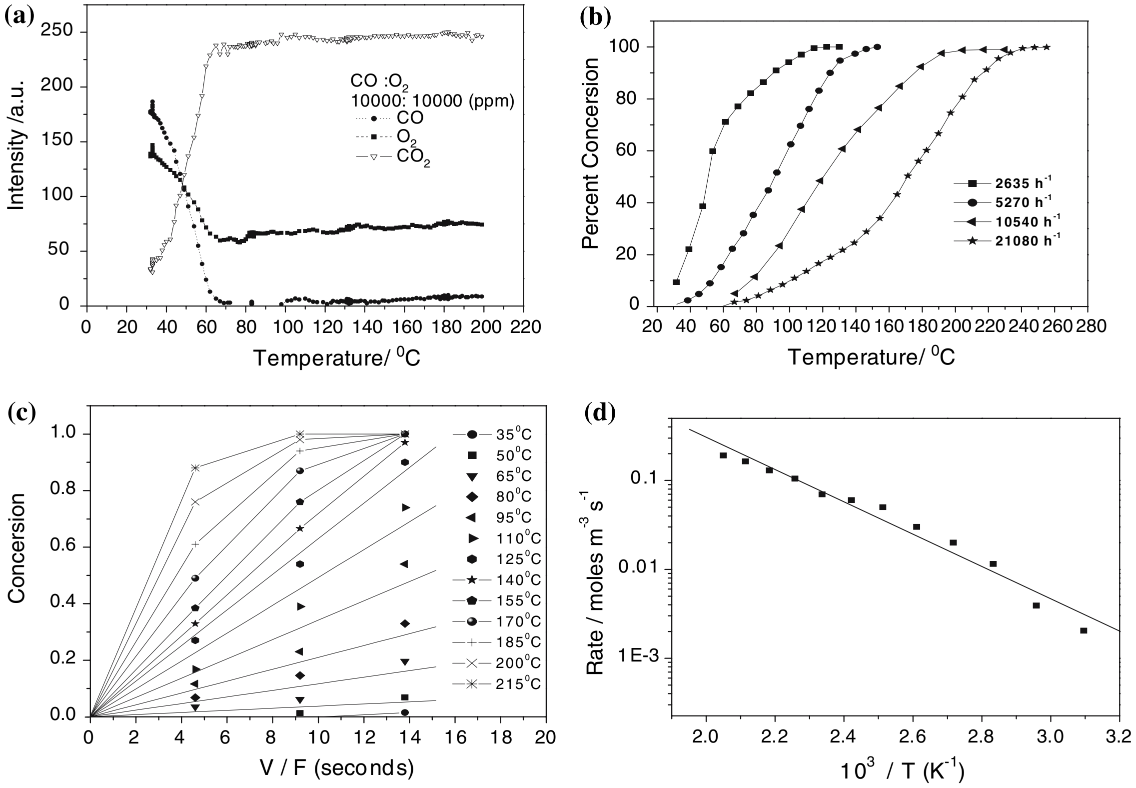

Figure 5. TPR profile over monolith for (a) 1vol% CO oxidation by 1vol% of $O_2$; (b) conversion of 2000 ppm CO with 2000 ppm of oxygen at different space velocity; (c) CO Oxidation of 2000 ppm of CO by 2000 ppm of oxygen at different resident time and (d) variation in ln(rate) versus inverse of temperature (Arrhenius plot) for CO oxidation.

Keeping in mind that amount of wash coat and metal loading in $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ grown monolithic catalyst is only 20–25% of the catalysts reported in the literature, temperatures at which 50% and 100% conversion of the reactants are taking place are lower or comparable to the studies reported above. Another noticeable factor in the performance of $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ is that conversion starts at much lower temperature giving low light off temperature.

NO reduction by CO with $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ coated honeycomb catalyst is shown in figure 6(a). Concentrations of both the reactants were 10,000 ppm. $N_2O$ and $CO_2$were analyzed by online GC. About 100% NO conversion occurs below 205 °C. In figure 6(b) $N_2O$, $CO_2$ and $N_2O + CO_2$ are plotted against the temperature. We see that $N_2$ selectivity obtained for the mass balance is 70% in the temperature range of 160 °C. About 100% $N_2$ selectivity is obtained above 220 °C. Rate of NO reduction comes out to be 0.011 moles $m^{-3}$ $s^{-1}$ at 100 °C.

Acetylene and ethylene are the major hydrocarbon constituents of the exhaust. Acetylene oxidation by $O_2$ has been carried out with 10,000 ppm of acetylene and 50,000 ppm for $O_2$. About 100% conversion of acetylene occurs at 240 °C (figure 7). Rate of acetylene oxidation is 0.012 moles $m^{-3}$ $s^{-1}$ at 200 °C.

Aging of the monolith catalyst does not show any decrease in its catalytic activity as the same catalyst has been tested several times for hours without re-conditioning. Further, monolith catalyst kept in air for

Table 1
Comparison between our monolithic catalyst and monolithic catalyst reported in the literature

| Catalyst | Metal loading (gm/L) | Washcoat loading (gm/L) | [CO] (vol%) | [O] (vol%) | SV ($h^{-1}$) | $T_{50}$ (°C) | $T_{100}$ (°C) |
|---|---|---|---|---|---|---|---|
| $Pd/Al_2O_3$ | 1.1 | 110 | 0.51 | 0.73 | 50,000 | 275 | 310(100%) |
| Pd--$Rh/Al_2O_3$ | 1.32 | " | " | " | " | 240 | 250(90%) |
| $Pd/Al_2O_3$-$CeO_2Pd - Rh/Al_2O_3$ - | 1.1 | " | " | " | " | 200 | 270(100%) |
| $CeO_2$(Reference (17) | 1.32 | " | " | " | " | 220 | 260(100%) |
| $Pd/Al_2O_3$ (Reference (21)) | 0.17 | 81.4 | 0.1 | 10 | 39,000 | 188 | 195(100%) |
| $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ (Present report) | 0.23 | 18.1 | 0.16 | 0.16 | 21,000 | 170 | 220(100%) |

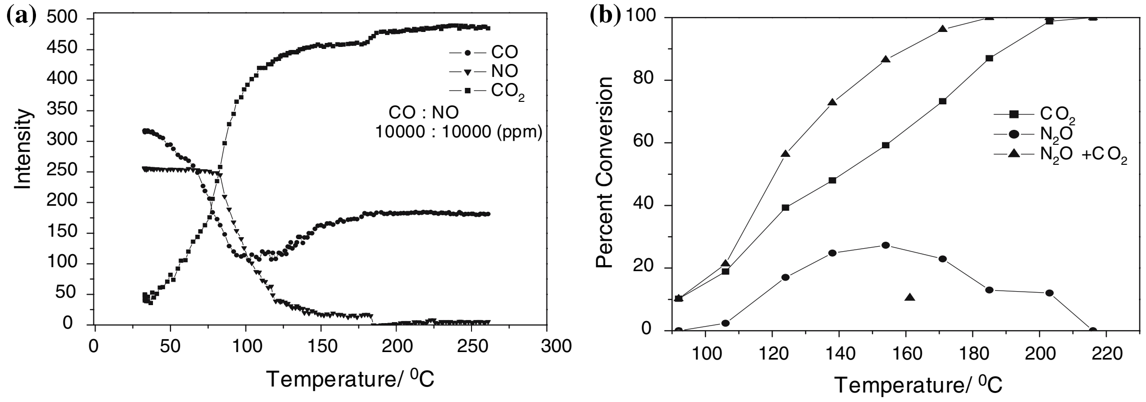

Figure 6. TPR profile over monolith for (a) 1 vol% NO conversion by 1 vol% CO and (b) $CO_2$, $N_2O$ and $CO_2 + N_2O$.

6 months, did not show any decrease in its catalytic performance. It indicates that the catalyst is stable in air and moisture.

Monolith was heated in air at 800 °C for 12 h and there was no decrease in the catalytic performance. However, heat treatment at 900 °C shows evaporation of the Pd metal. But same monolith can be recoated after washing in acid.

## 4. Three-way catalytic performance over $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ coated honeycomb catalyst

Three-way catalytic reactions with $Pd_{0.02}Ce_{0.98}O_{2-\delta}$ over honeycomb have been investigated. A gas mixture containing 10,000 ppm of CO, 2000 ppm of $C_2H_2$ , 2000 ppm of NO and 7000 ppm of $O_2$ is passed over the monolithic catalyst at a space velocity of 880 °C. Total reductants are equal to 15,000 ppm and total oxidants are equal to 16,000 ppm equivalent to [O]. 2000 ppm of NO gives 2000 equivalent of [O] and 7000 ppm of $O_2$ gives 14,000 ppm of [O]. Thus there is a small excess of 1000 ppm of [O]. Conversion profile is given in figure 7. CO and $C_2H_2$ are converted before NO conversion. NO is fully converted below 200 °C. Thus, under stoichiometric and even with ~15% excess oxygen the pollutants CO, NO and 'HC' (acetylene) are converted to $CO_2$, $N_2$ and $H_2O$ below 225 °C.

In this method of coating, composition of the catalyst can be varied very easily by taking desired amount of metal ions in the solution. $Ce_{1-x}Zr_xO_2$ can be made by taking the mixture of ceric ammonium nitrate and zirconium nitrate in the solution in desired ratio. Two or more metal ions, Pt, Pd and Rh, etc. can be taken for the substitution in the ceria or $Ce_{1-x}Zr_xO_2$ by dissolving metal nitrates or chlorides in the solution in the desired stoichiometry. The method is a general one and we have shown here only one specific catalyst.

## 5. Conclusion

We have demonstrated a novel method of growing a 3-way catalyst over the cordierite monolith by solution combustion method. Three-way catalytic performance of the catalyst prepared by this method is good at low temperatures and adhesion of the catalyst is strong. Method is less time consuming and precious metal

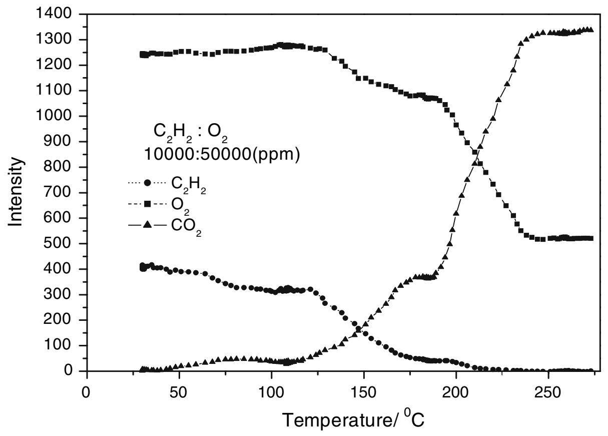

Figure 7. TPR profile over monolith for 1 vol% $C_2H_2$ oxidation by 5 vol% $O_2$.

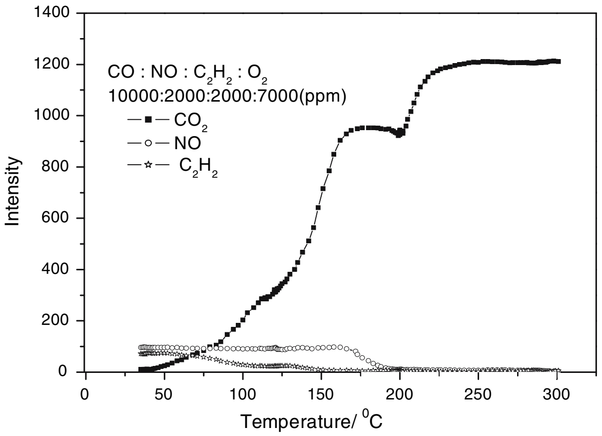

Figure 8. Three way catalytic performance over monolith for 10,000 ppm of CO, 2000 ppm of NO, 2000 ppm of $C_2H_2$ in presence of 7000 ppm of $O_2$.

loading is low compared to the commercial catalysts. Handling of nano oxide powder material is completely avoided in this method.

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