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REGULAR ARTICLE

High rates of catalytic hydrogen combustion with air over Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ coated cordierite monolith

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Abstract. Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ was coated on γ-Al$_2$O$_3$-coated honeycomb structured cordierite monolith (AHCM) by solution combustion method using dip-dry-heat process. This is a modified conventional method to coat the catalysts on honeycomb structured cordierite monolith (HCM). Formation of Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ on AHCM was confirmed by XRD. The XPS spectra of Pd(3d) core level confirmed Pd ion in Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ is in the form of +2 state. The surface morphology of coated catalyst was unchanged by long time exposure to hydrogen combustion reaction; i.e., H$_2$ + O$_2$ recombination reaction which indicated the stability of coating on monolith. Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ showed high rates of H$_2$ + O$_2$ recombination compared to 2 atom% Pd(metal)/γ-Al$_2$O$_3$, Ce$_{0.98}$Pd$_{0.02}$O$_{2-\delta}$, Ce$_{0.98}$Pt$_{0.02}$O$_{2-\delta}$, Ce$_{0.73}$Zr$_{0.25}$Pd$_{0.02}$O$_{2-\delta}$, Ti$_{0.99}$Pd$_{0.01}$O$_{2-\delta}$ and Ti$_{0.98}$Pd$_{0.02}$O$_{2-\delta}$. The activation energy of H$_2$ + O$_2$ recombination reaction over Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ is 7.8 kcal/mol. The rates of reaction over Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ at 60°C are in the range between 10 and 20 μmol/g/s. The rate of reaction over Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ increased with increase in the concentration of H$_2$. For 50 mL of H$_2$, it showed rates of the reaction around 36.45 μmol/g/s at room temperature and 230 μmol/g/s at 60°C. It was found that the rate of reaction due was lower due to hindering effect by adsorption of other gas molecules on the catalytic site. Finally, we propose a mechanism of hydrogen and oxygen recombination reaction over Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$.

Keywords. Solution combustion method; cordierite honeycomb; H$_2$ + O$_2$ recombination reaction; rate of conversion.

1. Introduction

Ever since Johann Wolfgang Dobereiner in 1823[1] and Michael Faraday in 1844[2] showed the formation of water on Pt, till now platinum metal has remained a catalyst for hydrogen combustion. Hydrogen combustion or H$_2$ + O$_2$ recombination reaction is a technologically important chemical reaction. Recycling of water in lead acid battery is a major issue in the maintenance of sealed lead acid battery.[3] Keeping H$_2$ concentration lower than 4.1% is crucial for nuclear power reactors.[4] Therefore, the finding of a new catalyst for H$_2$ + O$_2$ recombination reaction is important even today.

In H$_2$ + O$_2$ recombination reaction, the catalyst must decompose both H$_2$ and O$_2$. Hydrogen molecule can dissociate either by the addition of electron to antibonding orbital of H-H molecule producing H$_2^{\delta-}$-like species or by the removal of electron from bonding orbital to give H$_2^{\delta+}$-like species. In both H$_2^{\delta+}$ and H$_2^{\delta-}$, bond order is 1/2, meaning H-H bond is prone to dissociation. Such

a possibility of producing H$_2^{\delta-}$ and H$_2^{\delta+}$ species was shown by Datta *et al.*,[5] when H$_2$ exposed on Pt^{2+} ion in Ce$_{1-x}$Pt$_x$O$_{2-\delta}$, H$_2^{\delta+}$-like species was indeed observed by H^1-NMR studies. On the contrary, H$_2^{\delta-}$-like species was observed when H$_2$ was exposed on Pt metal particles. Here, Pt^{2+} ion receives electrons from H$_2$ molecule to form H$_2^{\delta+}$ and Pt metal donates electrons to H$_2$ molecule to form H$_2^{\delta-}$. Indeed, H$_2^{\delta+}$-like species was the key for high catalytic activity of H$_2$ + O$_2$ recombination over Pt^{2+} ion in Ce$_{1-x}$Pt$_x$O$_{2-\delta}$.

H$_2$ + O$_2$ recombination reaction has been done over Pd/Al$_2$O$_3$[6,7] and SiO$_2$-supported Pd-Pt catalyst[8] to investigate the high possible rates of catalytic reaction. Similarly, for H$_2$ + O$_2$ recombination reaction at room temperature, nearly 100 times more active catalyst was synthesized with Pt^{2+} ion in CeO$_2$ in the form of nano-crystalline Ce$_{1-x}$Pt$_x$O$_{2-\delta}$.[9] Interestingly, Pd^{2+} ion-substituted TiO$_2$, Ti$_{0.99}$Pd$_{0.01}$O$_{2-\delta}$ powder catalyst showed much higher catalytic properties for H$_2$ + O$_2$ recombination at 45°C and above compared to Pt^{2+} ion substituted CeO$_2$.[10] Usually, the heterogeneous catalytic gas phase reaction is carried out by passing gas mixture

over the fixed bed catalyst. Due to fine particle packing in fixed bed reactor, large pressure drop develops and it is difficult to carry out the gas phase reaction under this developed pressure. And during the gas phase reaction, powder catalyst is also carried away by the gas flow. But, these problems can be avoided by employing the catalyst coated on high surface area ceramic monolith supports.

Monolithic structures were developed in 1960s and 1970s for automotive applications because of their favourable properties such as, to bring large volume of gases into contact with a solid catalyst, a low pressure drop, a high geometric surface area, short diffusion lengths, high mechanical strength, high thermal stability, low thermal expansion coefficient and thermal shock resistance.[11,12] Luca *et al.*,[13] and Lachmann *et al.*,[14–17] summarized the different methods for synthesis of ceramic monoliths. Nijhuis *et al.*, reviewed the conversion of bare monolith body into a proper catalyst.[18] Boger *et al.,* also discussed the superior performance characteristics of honeycomb-shaped monolithic catalyst used in chemical industry.[19] Generally, a ceramic monolith is made up of cordierite material ($Mg_2Al_4Si_5O_{18}$) which is highly stable even upto 1000°C and it has low thermal expansion coefficient. Cordierite monolith is designed as a cylinder with square channelled cross section which looks like a honeycomb and hence, it is called as honeycomb structured cordierite monolith (HCM). There are many techniques for coating catalysts on the surface of ceramic monolith namely, colloidal coating,[20] sol-gel coating[21] and slurry coating.[22] However, loading nanocrystalline powder catalyst was difficult and a suitable method, if found, to coat on high surface area HCM, $Ti_{1−x}Pd_xO_{2−\delta}$ can become a commercially viable low temperature $H_2 + O_2$ recombination catalyst.

In an earlier study, Pd was dispersed in TiO_2 in ionic state and high catalytic activity for CO oxidation and hydrocarbon oxidation have been observed.[23] In present study, we expect high catalytic activity of $Ti_{0.97}Pd_{0.03}O_{2−\delta}$ catalyst coated AHCM on $H_2 + O_2$ recombination reaction. Results are compared with other catalysts, $Ti_{0.98}Pd_{0.02}O_{2−\delta}$, $Ti_{0.99}Pd_{0.01}O_{2−\delta}$, $Ce_{0.98}Pd_{0.02}O_{2−\delta}$, $Ce_{0.98}Pt_{0.02}O_{2−\delta}$, $Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2−\delta}$ and 2 atom% Pd/Al_2O_3 coated honeycombs.

2. Experimental

Since the bare monolith has smooth surface, it is necessary to coat a layer of material which increases surface area and bind chemically with the catalyst. This support material coating procedure is called wash coating. Usually, γ-Al_2O_3 or silica or carbon is wash coated on ceramic monolith.[24,25] Earlier, $Ce_{0.98}Pd_{0.02}O_{2−\delta}$ was coated on cordierite honeycomb for 3-way catalytic reaction by Sharma *et al.*[26,27] The same procedure was followed to coat $Ti_{1−x}Pd_xO_{2−\delta}$ and many other catalysts for $H_2 + O_2$ recombination reaction.

2.1 *Growing γ-Al_2O_3 on cordierite honeycomb by solution combustion method*

We have taken 3.5 cm diameter and 6 cm long cordierite honeycomb with 400 cells/inch.[2] γ-Al_2O_3 was coated on the cordierite ceramic honeycomb. An aqueous solution of stoichiometric amount of $Al(NO_3)_3$ and oxalyldihydrazide (ODH, $C_2H_6N_4O_2$) was prepared. Dried ceramic monolith was dipped in the solution and heated at 400°C. Thickness of the coating was built up by repeated dip-dry-heat procedure. Chemical reaction on the surface of HCM can be written as:

$$2Al(NO_3)_3 + 3(CONHNH_2)_2 \xrightarrow[400°C]{\Delta} \gamma\text{-}Al_2O_3$$
$$+ 6CO_2 + 9N_2 + 9H_2O \tag{1}$$
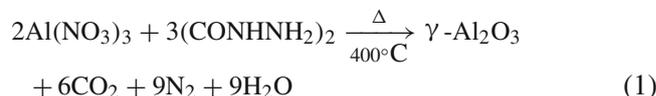
In fact, this is a good method of making γ-Al_2O_3.[28]

In a typical coating of γ-Al_2O_3, 10 mmol of $Al(NO_3)_3 \cdot 9H_2O$ (≥98%, Sigma-Aldrich) and 15 mmol of ODH (98%, Sigma-Aldrich) were dissolved in 20 mL of water. Honeycomb was dipped, dried and heated at 400°C. It must be noted that during the combustion reaction, γ-Al_2O_3 is formed and get coated on cordierite. A detailed study of epitaxial growth of γ-Al_2O_3 on cordierite surface has been studied. Adhesion of γ-Al_2O_3 on cordierite is due to γ-Al_2O_3 lattice growing on the lattice of cordierite oxide.[28] On ultrasonication, γ-Al_2O_3 does not come out. In this method, due to the growth of γ-Al_2O_3 on cordierite, it gets chemically bonded. On the contrary, slurry coating does not bond properly and it will come out under ultrasonication. Weight of γ-Al_2O_3 should be in the range 1–2% weight of honeycomb.

2.2 *Coating of catalysts over γ-Al_2O_3 coated cordierite monolith*

$TiO(NO_3)_2$, $PdCl_2$ (≥99.9%, Sigma-Aldrich) and glycine ($C_2H_5NO_2$, S. D. Fine Chemical Limited, India) are the precursors used for the synthesis of $Ti_{1−x}Pd_xO_{2−\delta}$. Initially, $TiO(NO_3)_2$ solution was prepared by hydration of titanium isopropoxide, $Ti(OC_3H_7)_4$ (97%, Sigma-Aldrich) followed by addition of nitric acid. In typical coating of $Ti_{0.97}Pd_{0.03}O_{2−\delta}$ (3 atom% Pd in TiO_2), 9.7 mmol of $TiO(NO_3)_2$, 0.3 mmol of $PdCl_2$ and 11 mmol of glycine are dissolved in 20 mL of water to make a solution. AHCM was dipped into the solution, dried and rapidly heated at 350°C. Dip-dry-heat is repeated to load 1–3% of catalyst weight with respect to honeycomb weight. Weight of the catalyst loaded in cordierite monolith is around 110 mg amounting to 1% monolith weight in this study. Chemical reaction on the surface of AHCM can be written as:
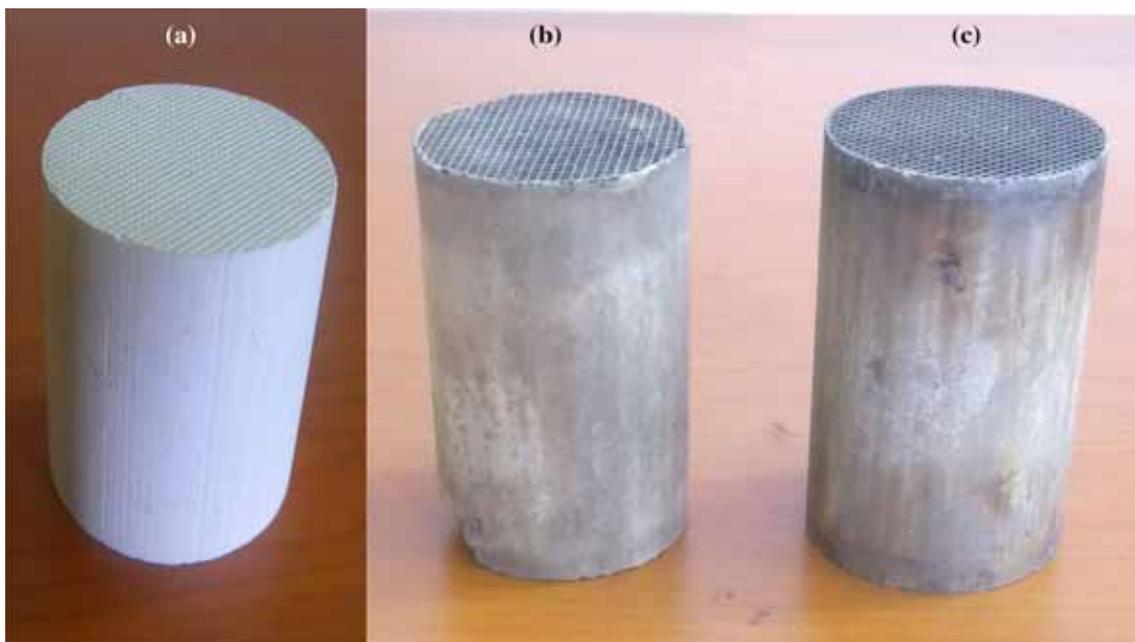
Figure 1. Photographs of (a) uncoated, and (b) coated $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ on AHCM and (c) after several cycles of reaction over $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ coated AHCM.
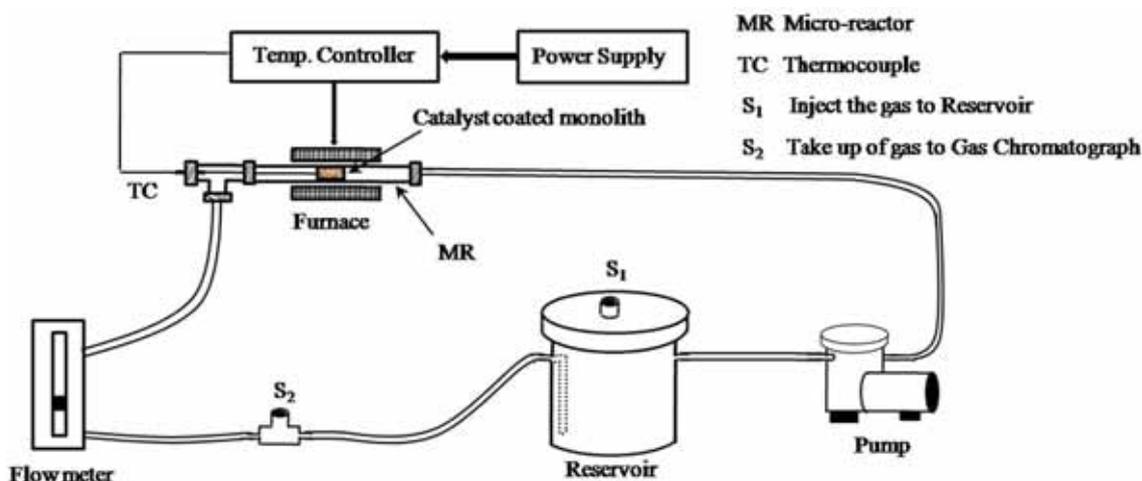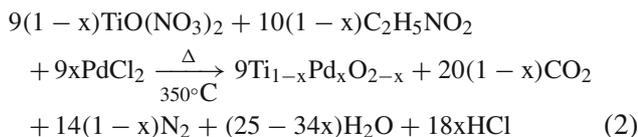

Figure 2. Schematic diagram of $H_2 + O_2$ recombination reaction setup.

$$9(1-x)TiO(NO_3)_2 + 10(1-x)C_2H_5NO_2$$
$$+ 9xPdCl_2 \xrightarrow[350°C]{\Delta} 9Ti_{1-x}Pd_xO_{2-x} + 20(1-x)CO_2$$
$$+ 14(1-x)N_2 + (25-34x)H_2O + 18xHCl \quad (2)$$

Similarly, we have coated $Ti_{0.98}Pd_{0.02}O_{2-\delta}$ (2 atom% Pd for Ti in TiO_2), $Ti_{0.99}Pd_{0.01}O_{2-\delta}$ (1 atom% Pd for Ti in TiO_2), $Ce_{0.98}Pd_{0.02}O_{2-\delta}$, $Ce_{0.98}Pt_{0.02}O_{2-\delta}$, $Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2-\delta}$ and 2% Pd/Al_2O_3 on ceramic monolith with corresponding precursors. For the synthesis of $Ti_{0.98}Pd_{0.02}O_{2-\delta}$, 9.8 mmol of $TiO(NO_3)_2$, 0.20 mmol of $PdCl_2$ and 10.9 mmol of glycine were taken in a 300 mL crystallizing dish and made into solution for dipping of AHCM. Repeated the dip-dry-heat procedure was followed till the required

weight of catalyst was coated on the surface of monolith. Similarly, 9.9 mmol of $TiO(NO_3)_2$ solution, 0.10 mmol for $PdCl_2$ and 11 mmol of glycine were taken for $Ti_{0.99}Pd_{0.01}O_{2-\delta}$. For coating of $Ce_{0.98}Pd_{0.02}O_{2-\delta}$, 9.8 mmol of $(NH_4)_2Ce(NO_3)_6$ (99%, Loba Chemie Private Limited, India), 0.20 mmol of $PdCl_2$ and 26.1 mmol of glycine were taken as the precursors. Solution was made using 20 mL of distilled water and continued the dip-dry-heat procedure. For $Ce_{0.98}Pt_{0.02}O_{2-\delta}$, 9.8 mmol of $(NH_4)_2Ce(NO_3)_6$, 0.20 mmol of $(NH_3)_4Pt(NO_3)_2$ (99.995%, Sigma-Aldrich) and 26.09 mmol of glycine were the precursors. AHCM was dipped into a solution made of 7.3 mmol of $(NH_4)_2Ce(NO_3)_6$, 2.5 mmol of $Zr(NO_3)_4 \cdot 5H_2O$ (Rolex Chemical Industries, India), 0.20 mmol of $PdCl_2$, 25.02 mmol of glycine mixture for coating

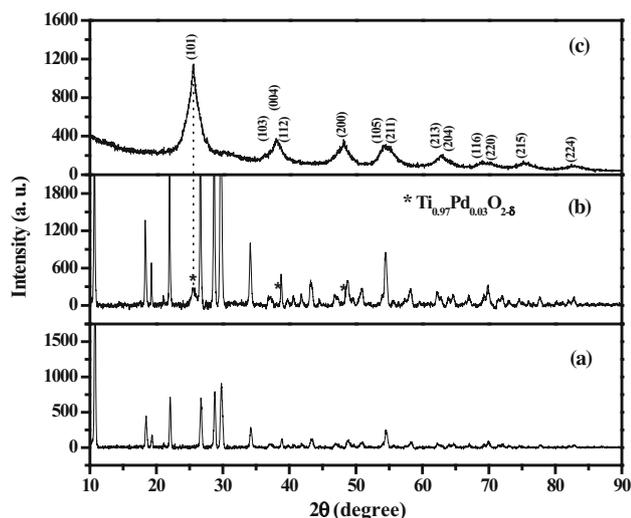**Figure 3.** Powder XRD patterns of (a) Cordierite ($Mg_2Al_4Si_5O_{18}$) honeycomb structure monolith, (b) $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ catalyst coated AHCM and (c) as pre-pared $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ powder.

$Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2-\delta}$ and heated it in the preheated muf-fle furnace at 350°C. For synthesis of 2 atom% Pd metal on γ-Al_2O_3, we have taken same amount of $PdCl_2$ as for the synthesis of $Ti_{0.98}Pd_{0.02}O_{2-\delta}$ and around 2 mmol of glycine in a crystallizing dish and coated on little excess γ-Al_2O_3-coated cordierite monolith by dip-dry-heat method. Resultant product is in the PdO form and so, it was reduced to Pd metal by dipping PdO coated monolith in 50% hydrazine hydrate solution (S.D. Fine Chemical Limited, India). After 2 h, honeycomb, which changed colour to black, was removed from the solution and dried at 60°C for an hour. Pd load-ing in each of the catalyst was maintained to the same extent of 3 atom% Pd in TiO_2 namely, $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ except for 1 and 2 atom% Pd in TiO_2. A fine powder of $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ was also synthesized for comparison. The photographs of uncoated and $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ catalyst coated AHCMs are shown in Figures 1(a) and 1(b). Structures of the catalyst coated on AHCM were determined by XRD and XPS studies.

XRD patterns were recorded using a Philips X'Pert diffrac-tometer with a scanning rate 0.5°/min with 0.017° step size

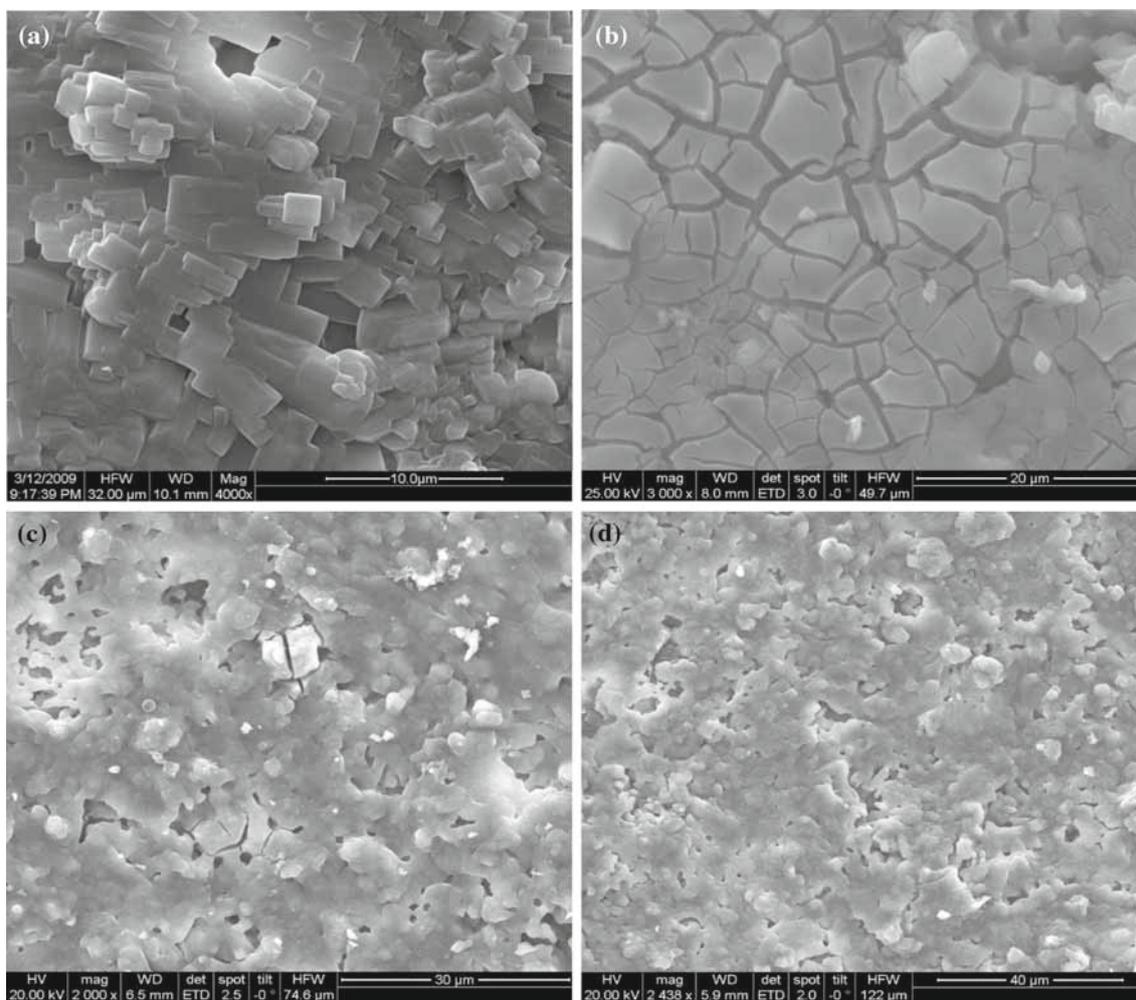**Figure 4.** Scanning Electron Microscopy (SEM) images of (a) HCM, (b) AHCM, (c) before and (d) after several cycles of $H_2 + O_2$ recombination reaction on $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ catalyst-coated AHCM.
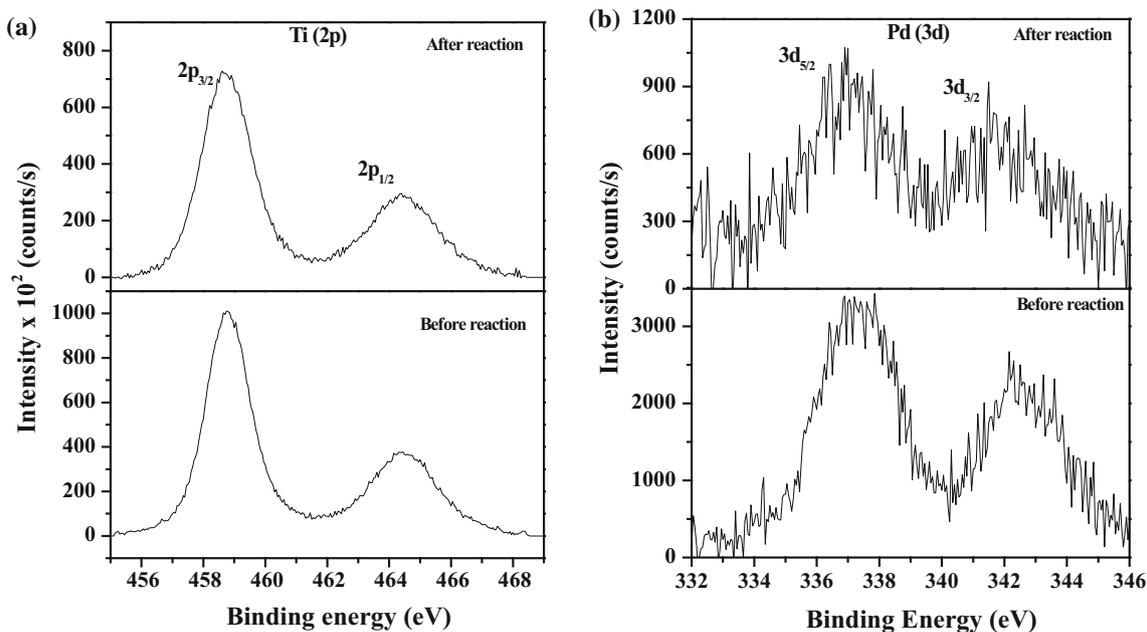
Figure 5. (a) Ti(2p) core level XPS and (b) Pd(3d) core level XPS of $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ coated on AHCM.

in the 2θ range 10–90°. X-ray photoelectron spectra were recorded by using Thermo Fisher Scientific Multilab 2000 instrument with Al K α (1486.6 eV) X-ray. C(1s) peak at 284.5 eV is the reference to other binding energy (BE) of core levels reported here.

Scanning electron microscope (SEM) was employed to examine the sample of the monolith before and after coating and also, before and after catalytic reaction. The surface images of the catalyst-coated monolith were recorded by FEI Quanta scanning electron microscope.

$H_2 + O_2$ recombination reaction is a highly exothermic.
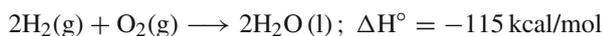
$$2H_2(g) + O_2(g) \longrightarrow 2H_2O\,(l)\,;\ \Delta H° = -115\,\text{kcal/mol} \tag{3}$$

Hence, it is necessary to develop the reactor which can overcome the problem of heating in the gas flowing condition so that during the catalytic reaction surface temperature of catalyst does not increase. The circulation of gas with high flow rate is one way to overcome the problem. Therefore, we designed the closed cycle system for $H_2 + O_2$ recombination reaction and the schematic diagram is shown in Figure 2. It consists of a pump to circulate the gas mixtures, 2000 mL capacity reservoir to fill up the excess of air for the experiment, a flow meter to measure the flow rate by the pump, a sampling port to take the gas mixture for gas sampling into Gas Chromatography (GC), a port to inject H_2, a reactor of 3.8 cm inner diameter quartz tube having the catalyst-coated AHCM and furnace with temperature controller. Temperature was measured by using of K-type chromel-alumel thermocouple. Hydrogen gas was introduced through an inject port, S_1 which is on the top of the reservoir.
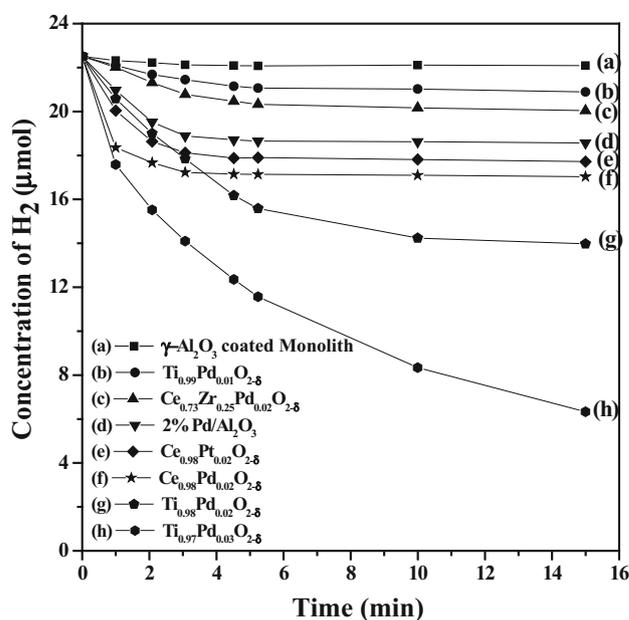

Figure 6. $H_2 + O_2$ recombination reaction over the various catalysts at room temperature. (0.5 mL of H_2, RT = 30°C).

Reaction was done by injecting a small quantity of pure H_2 by a fine needle through the port, S_1 to reservoir in which was filled with air. After one minute of circulation, gas was sampled at S_2 and injected into the GC. Flow rate was 2000 mL/min and thus, if 2 mL of H_2 was injected into the reservoir, then H_2 flow is equal to 2 mL/min. H_2 concentration was measured by GC at regular interval of time. Reaction was carried out at higher temperature by temperature controller.
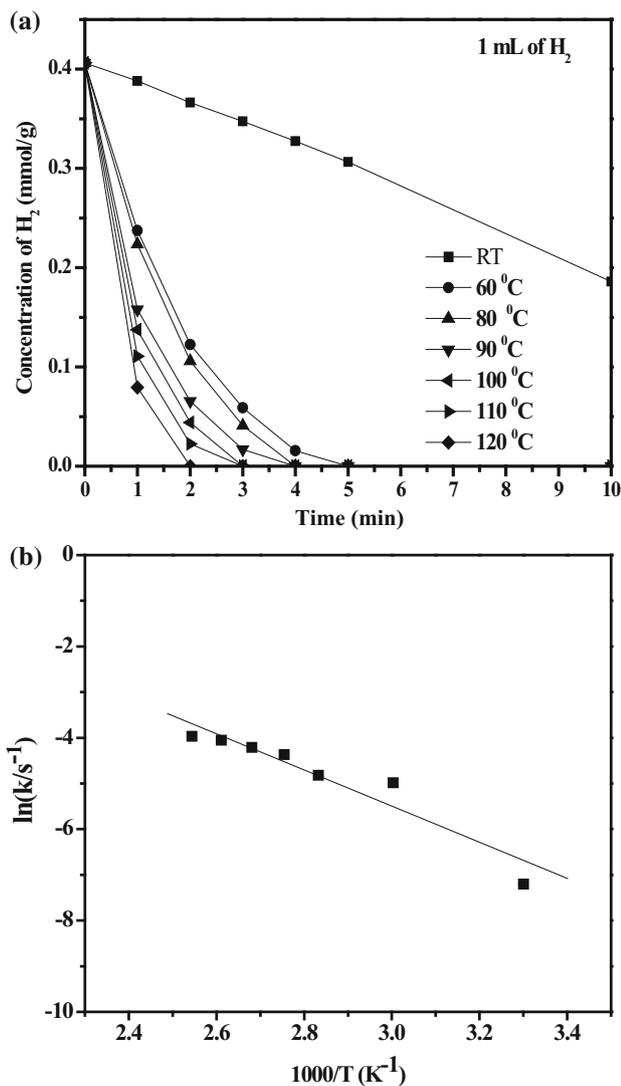
Figure 7. (a) $H_2 + O_2$ reaction over $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ at different temperatures (1 mL of H_2). (b) $\ln(k/s^{-1})$ vs $1/T$ (K^{-1}) plot for $H_2 + O_2$ recombination reaction.

Figure 8. $H_2 + O_2$ recombination reaction over $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ for different volumes (a) at room temperature and (b) at 60°C.

3. Results and Discussion

3.1 *XRD study*

X-ray diffraction pattern of bare cordierite is given in Figure 3(a). This XRD pattern is corresponding to orthorhombic structure with *Cccm* space group and the lattice parameters are a = 17.0470 Å, b = 9.7315 Å and c = 9.3463 Å (JCPDS No. 1-082-1541). Because γ-Al_2O_3 coating on cordierite monolith is very thin, XRD lines due to γ-Al_2O_3 are not identified. XRD of active phase $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ grew on AHCM surface is given in Figure 3(b). In addition to the lines due to cordierite, XRD lines of $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ are observed in anatase structure. Powder XRD pattern of $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ synthesized by combustion method is given in Figure 3(c)
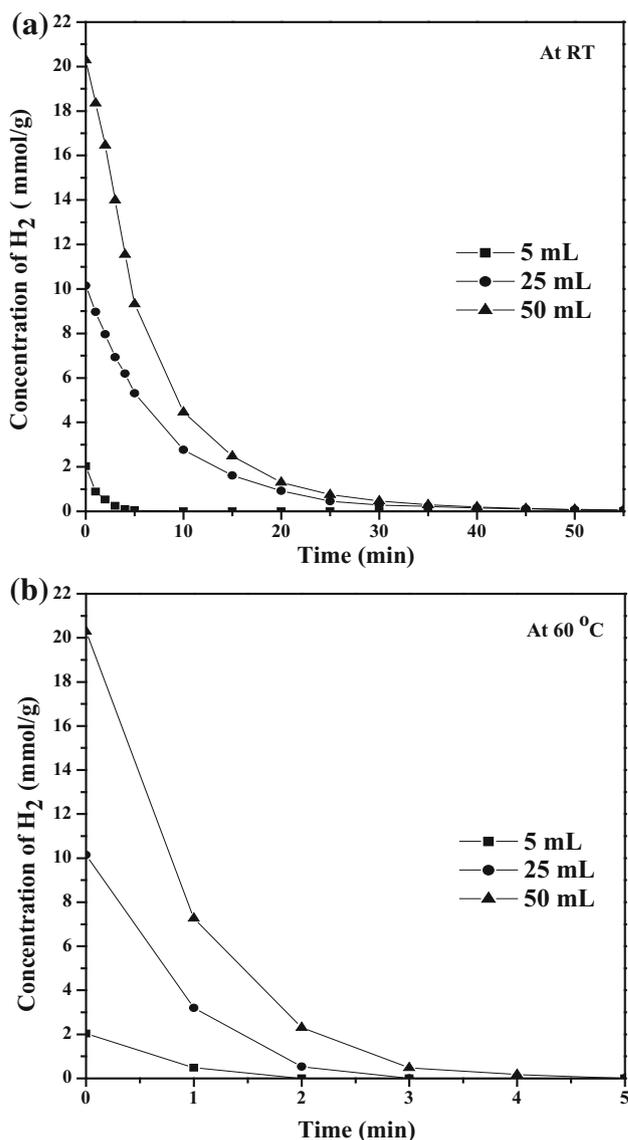
for comparison. XRD lines are indexed to anatase TiO_2 (Tetragonal, $I4_1/amd$, JCPDS No. 21-1272). The position of lines match exactly in Pd ion-substituted TiO_2, confirming catalyst phase-coated on monolith. Phase of other catalysts coated on AHCM have been confirmed by XRD studies.

3.2 *SEM study*

In Figure 4(a–d), SEM images of bare HCM, AHCM, $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ catalyst-coated on AHCM and after several cycles of reaction on catalyst-coated monolith are shown, respectively. In Figure 4(a), we can see the surface of cordierite monolith and macropores on the surface of monolith. After γ-Al_2O_3 coating

on bare monolith, all the macropores were completely covered by γ-Al$_2$O$_3$ material, which is shown in Figure 4(b). γ-Al$_2$O$_3$ was coated uniformly on the surface of ceramic monolith with the thickness of around 200–250 nm as seen from cross-section. Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ catalyst was uniformly coated on surface of γ-Al$_2$O$_3$-coated honeycomb which can be seen in Figure 4(c). Finally, we confirmed that catalyst coated surface is very strongly bound on the wash-coated surface by ultrasonic test.

3.3 *XPS study*

XPS of Ti(2p) core level recorded from the surface of Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$-coated AHCM before and after catalytic reaction are shown in Figure 5(a). Ti is in +4 state and the binding energies of Ti(2p$_{3/2}$) and Ti(2p$_{1/2}$) are 458.8 eV and 464.5 eV, respectively. Binding energies of Ti(2p) core level are exactly the same that of in Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ powder.[23] In Figure 5(b), XPS of Pd(3d) core level of Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$-coated on honeycomb before and after H$_2$ + O$_2$ recombination reaction are shown. Binding energies of Pd(3d$_{5/2}$) and Pd(3d$_{3/2}$) of Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ coated on AHCM are 337.4 eV and 342.4 eV, respectively. Binding energy of Pd(3d$_{5/2}$) peak in Pd metal and PdO are observed at 335.1 eV and 336.4 eV, respectively.[29] Therefore, the oxidation state of Pd in Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$which coated on monolith is +2. Since the binding energy of Pd^{2+} ion in TiO$_2$ matrix is higher than that of in PdO, Pd^{2+} ion is more ionic than PdO. Binding energies of Pd(3d) core level of Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$-coated on honeycomb are exactly same as in Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ powder.[23] The oxidation state of Pd ion will be in +2 state, but not +4 state in Ti$_{1-x}$Pd$_x$O$_{2-\delta}$, as was found by the extensive studies on Pd earlier.[30]

3.4 *H$_2$ + O$_2$ recombination reaction*

0.5 mL of pure H$_2$ was injected into the 2 L reservoir and circulated over a single monolith at a flow rate of 2 L/min. At one minute interval, H$_2$ was sampled and H$_2$ content was analyzed by GC. This procedure was followed for all the catalysts. Hydrogen conversion in presence of air over various catalysts is shown in Figure 6. There was no reaction by AHCM as seen from Figure 6(a). Other catalysts like Pd and Pt ion substitution in CeO$_2$ showed moderate rate of conversion. 2 atom% Pd metal on γ-Al$_2$O$_3$ showed moderate conversion. But, Pd ion substitution in TiO$_2$ showed highest conversion with time. Increase in the conversion was observed with increase in Pd^{2+} ion from 1% to 3% in TiO$_2$. H$_2$ + O$_2$ recombination reaction over 1%, 2% and 3% Pd ion substitution in TiO$_2$
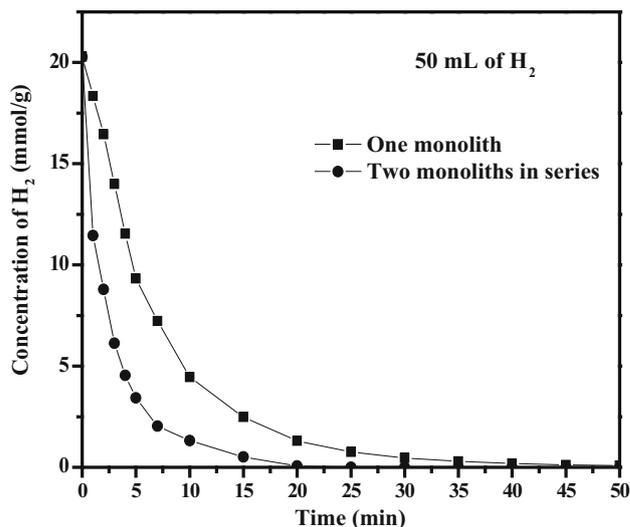
Figure 9. H$_2$ + O$_2$ recombination reaction over two series of Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ coated monoliths with 50 mL of H$_2$ at room temperature (30°C).

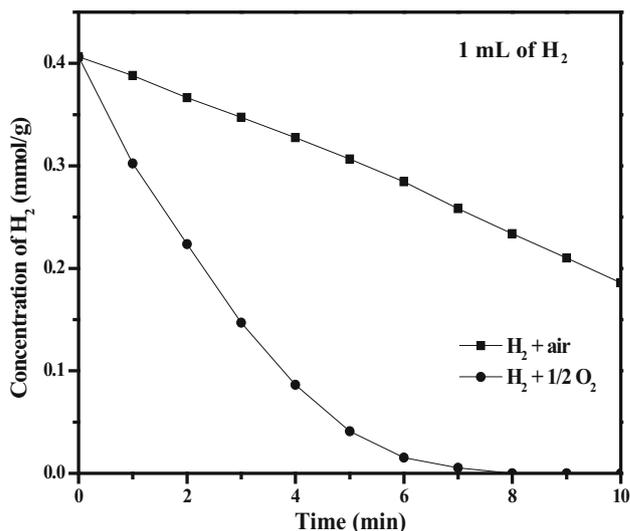**Figure 10.** H$_2$ + O$_2$ reaction over Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ in presence of O$_2$ (H$_2$: O$_2$ :: 2:1) and air at room temperature (1 mL of H$_2$).

are denoted as (b), (g) and (h), respectively in Figure 6. Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ showed highest rate of reaction compared to other catalysts at room temperature and so, we chose this catalyst for further study. Except Ti$_{1-x}$Pd$_x$O$_{2-\delta}$, the monoliths contained same amount of Pd as in Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ coated monolith. Clearly, Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ coated AHCM showed highest activity.

In Figure 7(a), H$_2$ + O$_2$ recombination reaction over Ti$_{0.97}$Pd$_{0.03}$O$_{2-\delta}$ at different temperatures are shown. This graph was plotted with hydrogen concentration per gram of palladium in catalyst versus time. At room temperature, 22 mmol of H$_2$ was converted into water after 10 min of reaction. In the catalytic reaction at higher
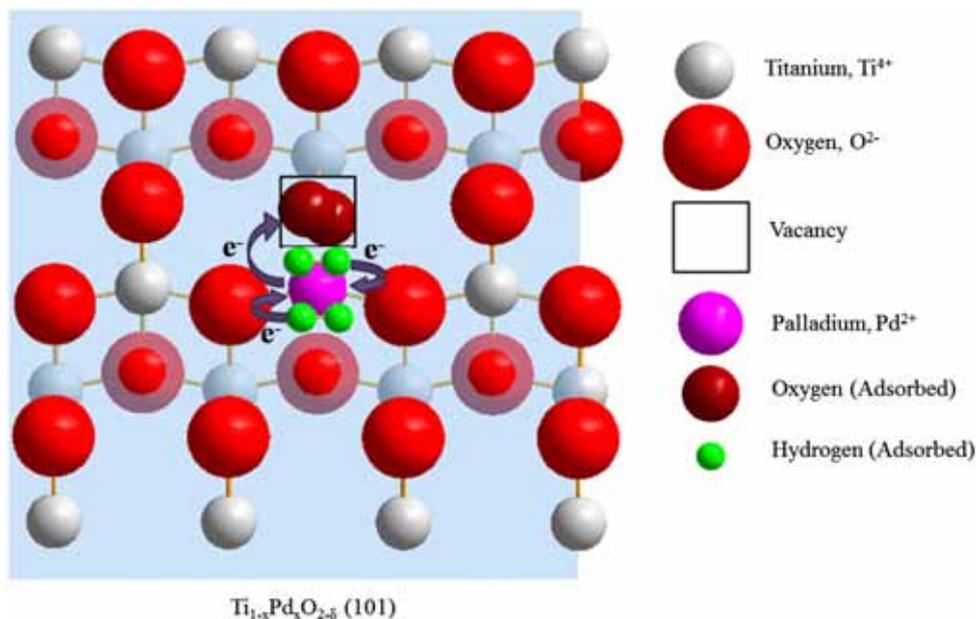
$Ti_{1-x}Pd_xO_{2-\delta}$ (101)

Figure 11. Schematic diagram of $H_2 + O_2$ recombination reaction mechanism on the surface of $Ti_{0.97}Pd_{0.03}O_{2-\delta}$.

temperature, 44 μmol of H_2 conversion occurred within 5 min. Time required to 100% conversion of H_2 at 60, 80, 90, 100, 110 and 120°C were 5, 4, 3.5, 3, 2.5 and 2 minutes, respectively. With increase in the temperature of the reactor, rate of reaction was also increased. By initial slope method, we calculated the rate constant, k. $\ln(k/s^{-1})$ vs 1/T (K^{-1}) plot for $H_2 + O_2$ recombination reaction at different temperatures is shown in Figure 7(b) and activation energy from the slope of $\ln(k/s^{-1})$ vs 1/T (K^{-1}) plot was calculated as 7.8 kcal/mol.

$H_2 + O_2$ recombination reaction over $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ with different concentrations of H_2 at room temperature and at 60°C are shown in Figures 8(a) and (b), respectively. At room temperature, the rates of the reaction for 5, 25 and 50 mL of H_2 are 9.20, 16.48 and 36.45 μmol/g/s, respectively. We observed that for increasing concentration of H_2, rate of the reaction is also increasing. This may be because surface temperature of the catalyst increases with increasing initial concentration. However, it is difficult to measure surface temperature of ceramic monolith. At 60°C, the rates of reaction for 5, 25 and 50 mL of H_2 are 26, 110 and 230 μmol/g/s, respectively. These values are very high compared to other compounds like $Ti_{0.99}Pd_{0.01}O_{2-\delta}$ and $Ce_{0.98}Pt_{0.02}O_{2-\delta}$.[9,10]

In Figure 9, $H_2 + O_2$ recombination reaction carried out over a series of two monoliths at room temperature. Each monolith has approximately same weight of catalyst. 2.2 mmol of H_2 was completely reacted with air within 50 and 20 min over a single monolith and a series of two monoliths respectively. Rates of reaction in both cases are similar.

We have carried experiments to find the hindering effect by other adsorbing molecule to lower the catalytic reaction. The mixture of H_2 and O_2 in the ratio of 1:1/2 is injected into the reservoir which the closed circular system was filled by Ar and carried out the reaction at room temperature. $H_2 + O_2$ recombination reaction by air and pure O_2 are shown in Figure 10. Surprisingly, stoichiometric $2H_2 + O_2$ recombination reaction with 1:1/2 mL of H_2:O_2, rate was higher than with 1 mL of H_2 in 2 litres of air or $\sim$ 418 mL of O_2. Initial amounts which 1 mL of H_2 injected in 2 litres is 500 ppm and impurity gases in the air can be 10 to 30% of this volume. Therefore, decrease in the rate of reaction in air can be due to inhibit effect by HC and CO_2 in air.

After several cycles of $H_2 + O_2$ recombination reaction carried out on the surface of the catalyst-coated AHCM, there was no change on surface morphology, which was confirmed by SEM image (Figure 4(d)) and photograph of several times exposed honeycomb (Figure 1(c)). After the $H_2 + O_2$ recombination reaction, there were no changes in the binding energies of Ti(2p) and Pd(3d) core levels (Figures 5(a) and (b)). Thus, Ti is stable in +4 state and Pd is stable in + 2 state even after several cycles of catalytic reaction. These results indicated the stability of $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ catalyst as well as the coating on the cordierite monolith.

Volume of the honeycomb of 3.5 cm diameter and 6 cm height is 57.5 cm³ and taking 50% as the void, volume of the catalyst bed is 28.75 cm³. Accordingly, 2000 mL/min flow over this catalyst gives space velocity of $4174\,h^{-1}$. This gives the residence time of 0.86 s. Thus,

this space velocity is sufficiently high with the residence time over catalyst bed of less than 1 sec. Under this condition, rates in the range of 10–20 µmol/g/s are quite high.[10] Therefore, the result on $H_2 + O_2$ recombination over $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ is indeed far better in terms of rate at high space velocity and at low activation energy.

A mechanism of $H_2 + O_2$ recombination reaction over $Ti_{0.97}Pd_{0.03}O_{2-\delta}$ is shown in Figure 11. There are two active sites for the catalytic reaction; one is Pd ion and another is oxide ion vacancy which is created due to the presence of +2 ion state of Pd in Ti^{4+} ion lattice.[23] Two molecules of H_2 adsorb on Pd ion and in the presence of O_2, O_2 molecule adsorbs in oxide ion vacancy. In the interval, electrons are exchanging between H_2 molecule to Pd^{2+} ion, and Pd^{2+} ion to adsorbed O_2 molecule. Finally, $2 H_2O$ molecules are formed and desorbed leaving behind again oxide ion vacancy and Pd ion in +2 state.

4. Conclusions

Catalyst coating on cordierite monolith is a good technique for various catalytic reactions. Coating technique overcomes the pressure drop effect as well as the loss of the catalyst in the reaction and it showed very high rates of reaction compared to $Ti_{0.99}Pd_{0.01}O_{2-\delta}$, $Ti_{0.99}Pd_{0.01}O_{2-\delta}, Ce_{0.98}Pd_{0.02}O_{2-\delta}, Ce_{0.98}Pt_{0.02}O_{2-\delta}, Ce_{0.73}$ $Zr_{0.25}Pd_{0.02}O_{2-\delta}$ and 2 atom% Pd/Al_2O_3. So, $Ti_{0.97}Pd_{0.03}$ $O_{2-\delta}$ catalyst-coated monolith will solve the problem which arises from hydrogen in nuclear power reactor and lead acid battery.

Acknowledgements

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