# Sonochemical synthesis of $Ce_{1-x}Fe_xO_{2-\delta}$ ( $0 \le x \le 0.45$ ) and $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$ nanocrystallites: oxygen storage material, CO oxidation and water gas shift catalyst<sup>†</sup>

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Nanocrystalline  $Ce_{1-x}Fe_xO_{2-\delta}$  ( $0 \le x \le 0.45$ ) and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  of ~ 4 nm sizes were synthesized by a sonochemical method using diethyletriamine (DETA) as a complexing agent. Compounds were characterized by powder X-ray diffraction (XRD), X-ray photo-electron spectroscopy (XPS) and transmission electron microscopy (TEM).  $Ce_{1-x}Fe_xO_{2-\delta}$  ( $0 \le x \le 0.45$ ) and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  crystallize in fluorite structure where Fe is in +3, Ce is in +4 and Pd is in +2 oxidation state. Due to substitution of smaller Fe<sup>3+</sup> ion in CeO<sub>2</sub>, lattice oxygen is activated and 33% Fe substituted CeO<sub>2</sub> *i.e.*  $Ce_{0.67}Fe_{0.33}O_{1.835}$ reversibly releases 0.31[O] up to 600 °C which is higher or comparable to the oxygen storage capacity of CeO<sub>2</sub>–ZrO<sub>2</sub> based solid solutions (*Catal. Today* **2002**, *74*, 225–234). Due to interaction of redox potentials of Pd<sup>2+/0</sup>(0.89 V) and Fe<sup>3+/2+</sup> (0.77 V) with Ce<sup>4+/3+</sup> (1.61 V), Pd ion accelerates the electron transfer from Fe<sup>2+</sup> to Ce<sup>4+</sup> in Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub>, making it a high oxygen storage material as well as a highly active catalyst for CO oxidation and water gas shift reaction. The activation energy for CO oxidation with Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub> is found to be as low as 38 kJ mol<sup>-1</sup>. Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.835</sub> and Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub> have also shown high activity for the water gas shift reaction. CO conversion to CO<sub>2</sub> is 100% H<sub>2</sub> specific with these catalysts and conversion rate was found to be as high 27.2 µmoles g<sup>-1</sup> s<sup>-1</sup> and the activation energy was found to be 46.4 kJ mol<sup>-1</sup> for Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub>.

# 1. Introduction

Synthesis of ceria-based solid solutions with controllable particle size and dopant concentration is of fundamental significance because of potential applications in oxide ion conductivity,<sup>1</sup> exhaust-catalysis,<sup>2,3</sup> water gas shift (WGS) catalysis,<sup>4</sup> fuel cells,<sup>5</sup> solar cells,<sup>6</sup> semiconductor devices and phosphor.<sup>7,8</sup> CeO<sub>2</sub> is utilized as a promoter in exhaust catalysis as it can release a high proportion of its lattice oxygen for CO and hydrocarbon oxidation under fuel rich conditions. Thus a multi-component catalyst with noble metals Pt, Pd, Rh impregnated on silica or Al<sub>2</sub>O<sub>3</sub> along with oxygen storage materials forms an auto exhaust catalyst.<sup>9-12</sup> The amount of lattice oxygen that can be reversibly exchanged from CeO<sub>2</sub> is called oxygen storage capacity (OSC).<sup>13</sup> However, the OSC of ceria can be enhanced by isovalent and aliovalant metal ion substitution in CeO<sub>2</sub>, in the form of solid solutions Ce<sub>1-x</sub>Zr<sub>x</sub>O<sub>2</sub>,<sup>14,15</sup> Ce<sub>1-x</sub>Ti<sub>x</sub>O<sub>2</sub>,<sup>16,17</sup> Ce<sub>1-x</sub>Sn<sub>x</sub>O<sub>2</sub>,<sup>18,19</sup> Ce<sub>1-x</sub>Cr<sub>x</sub>O<sub>2+δ</sub><sup>20</sup> and Ce<sub>1-x</sub>Ru<sub>x</sub>O<sub>2-δ</sub>.<sup>21</sup>

Higher OSC of  $Ce_{2/3}Cr_{1/3}O_{2.11}^{20}$  and  $Ce_{0.9}Ru_{0.1}O_{2-\delta}^{21}$  nanocrystallites than  $Ce_{0.5}Zr_5O_2^{22}$  at lower temperature is attributed to interaction of redox couples of  $Cr^{3+/4+/6+}$ ,  $Ru^{4+/3+/0}$  with  $Ce^{4+/3+}$  in their respective solid solutions. For example in  $Ce_{2/3}Cr_{1/3}O_{2.11}$ , in the  $H_2$  reduction step first  $Cr^{4+/6+}$  is reduced to  $Cr^{3+}$  and due to lower redox potential of  $Cr^{6+}/Cr^{3+}(1.33 \text{ V})^{23}$  compared to  $Ce^{4+}/Ce^{3+}(1.61 \text{ V})$ ,  $^{23}Cr^{3+}$  is oxidized to  $Cr^{6+}$  by  $Ce^{4+}$  reduction to  $Ce^{3+}$  state.  $Ce^{3+}$  ion is oxidized to  $Ce^{4+}$  by feed oxygen to regenerate  $Ce_{2/3}Cr_{1/3}O_{2.11}$ . Similarly OSC of  $Ce_{1-x}Zr_xO_2$  is higher

than  $Ce_{1-x}Ti_xO_2$  but  $Ce_{1-x-y}Ti_xPd_yO_{2-\delta}^{17}$  is reported to show higher activity for CO oxidation and NO reduction by CO compared to  $Ce_{1-x-y}Zr_xPdyO_{2-\delta}^{24}$  and  $Ce_{1-x}Pd_xO_{2-\delta}^{25,26}$  Higher activity of  $Ce_{1-x-y}Ti_xPd_yO_{2-\delta}$  is attributed to the synergistic interaction between  $Pd^{2+/0}$ ,  $Ti^{4+/3+}$  and  $Ce^{4+/3+}$  redox couples.<sup>17,24</sup>

As redox potential of  $Fe^{3+/2+}$  (0.77 V)<sup>27</sup> is lower compared to  $Ce^{4+/3+}$  (1.61 V),<sup>23</sup> Fe<sup>3+</sup> ion substituted ceria can be another promising candidate for higher OSC material as well as threeway exhaust catalyst in the presence of noble metal ions. Indeed  $Ce_{0.89}Fe_{0.1}Pd_{0.01}O_{2-\delta}$  synthesized by solution combustion method showed high OSC and catalytic activity for CO oxidation.<sup>28</sup> 15-20% Fe substituted CeO<sub>2</sub> also synthesized by template route showed high conversion for ethanol steam reforming.<sup>29</sup> Fe<sup>3+</sup> ion could be the cheapest substituent for Ce<sup>4+</sup> ion in CeO<sub>2</sub>. Thus higher substitution of Fe<sup>3+</sup> ion for Ce<sup>4+</sup> in ceria will reduce the cost of the OSC material and will increase the OSC of ceria. But only up to 10% Fe could be substituted by solution combustion method,<sup>28</sup> up to 15% by hydrothermal method<sup>30,31</sup> and up to 20% Fe<sup>3+</sup> ion is substituted by nitrate-citrate gel method.<sup>32</sup> Therefore we considered it worthwhile to find an alternate method to substitute higher % of Fe ion in CeO<sub>2</sub> even to the extent of 50%. We have designed a new low temperature sonochemical method to synthesize higher % Fe  $^{3+}$  and Pd  $^{2+}$  substituted ceria. An earlier sonication route was employed by Yin et al. to synthesized CeO<sub>2</sub> nanoparticles.33

Here we report synthesis, OSC, CO oxidation and WGS activity of  $Ce_{1-x}Fe_xO_{2-\delta}$  ( $0 \le x \le 0.45$ ) and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  nanocrystallites. Compounds were synthesized by sonochemical method using diethylenetriamine (DETA) as complexing agent.  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  shows higher OSC at lower temperature than  $Ce_{0.5}Zr_{0.5}O_2^{22}$  and both  $Pd^{2+}$  and  $Fe^{3+}$  ion substituted  $CeO_2$  *i.e.* 

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 $Ce_{\scriptscriptstyle 0.65}Fe_{\scriptscriptstyle 0.33}Pd_{\scriptscriptstyle 0.02}O_{\scriptscriptstyle 2-\delta}$  show high CO oxidation and WGS reaction activity.

## 2. Experimental

 $Ce_{1-x}Fe_xO_{2-\delta}$  (x = 0, 0.15, 0.25, 0.33 and 0.45) solid solutions were synthesized by sonication method from the starting materials,  $(NH_4)_2Ce(NO_3)_6$  (CAN), Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O and DETA by taking them in a molar ratio of 1-x : x : 3. For the synthesis of  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$ , 6.7 mmol of CAN is dissolved in 20 ml of distilled water and 3.3 mmol Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was dissolved in 5 ml of water, both the solutions were mixed and 30 mmol (3.4 ml) of DETA was added to it. The solution turned into brown colored gel immediately. The gel was kept under sonication (Oskar O U 9 equipped with high intensity piezoelectric resonator, 30 kHz, 100 W cm<sup>-2</sup>) for 8 h. The temperature of the solution reached up to 80 °C during sonication. The precipitated brown colored solid was filtered, washed in hot distilled water and dried in a hot air oven at 110 °C for 3 h. Similarly, for the preparation of Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>2-\delta</sub>, 6.5 mmol of CAN and 0.2 mmol of Pd(NO<sub>3</sub>)<sub>2</sub>·4H<sub>2</sub>O were dissolved in 20 ml of distilled water and 3.3 mmol Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O was dissolved in 5 ml of water. The solutions were mixed and 30 mmol or 3.4 ml of DETA was added. The resulting gel after DETA addition was kept under sonication for 8 h. The resulted solid obtained after the filtration and drying was brown in color.

X-ray diffraction (XRD) patterns of powders were recorded in a Phillips X'Pert diffractometer using Cu-K $\alpha$  radiation at scan rate of 0.2° min<sup>-1</sup> with 0.01° step size in the 2 $\theta$  range between 10 to 90°. Cu-K $_{\beta}$  radiation was filtered with a graphite crystal post monochromator. Structures were refined by Rietveld method, using FullProf-fp2k program<sup>34</sup>

For transmission electron microscopy (TEM), a toluene dispersion of the sample was dropped onto the holeycarbon coated Cu grids and images were recorded with FEI Technai 20 at 200 kV. EDX analysis was also carried out with the probe connected with TEM instrument. X-ray Photo-electron Spectra (XPS) of selected samples were recorded in a Thermo Scientific Multilab 2000 instrument using Al-K $\alpha$  at 150 W. Binding energies reported here are with reference to C(1 s) at 284.5 eV and are accurate within ±0.1 eV. UV-visible spectra of solid samples were recorded in by Perkin Elmer's LAMBDA 35 UV-visible spectrometer. BaSO<sub>4</sub> was used for baseline correction.

Oxygen storage/release properties or OSC of  $Ce_{1-x}Fe_xO_{2-\delta}$  were studied by hydrogen intake measurements carried out in a microreactor (30 cm length and 0.4 cm internal diameter) employing 5.49% H<sub>2</sub>/Ar (Chemix, Bangalore, India) with 30 sccm flow rate and at a linear heating rate of 10 °C min<sup>-1</sup>, up to 550 °C. Amount of H<sub>2</sub> consumption or equivalent [O] release or OSC of material is calibrated against hydrogen intake/consumption against known weight of CuO. OSC of material was also determined by direct oxidation of CO with compound in absence of external/feed oxygen. Powder catalyst was made into pressed granules of 40-80 mesh sizes to load in the micro reactor of length 30 and 0.4 cm internal diameter. Calibrated 10% CO/N<sub>2</sub>, 10%  $O_2/N_2$ , ultra high pure UHP N<sub>2</sub>, (UHP) H<sub>2</sub>, and UHP CO<sub>2</sub> (Chemix, Bangalore India) were used for CO oxidation and WGS reaction. Direct CO oxidation from the materials were investigated in a similar microreactor employing 1 vol% CO balanced in N2 with

total gas flow of 100 sccm over 200 mg of oxide sample, at a linear heating rate of 10 °C min<sup>-1</sup> up to 600 °C. CO oxidation over the catalysts are carried out with 200 mg of the catalyst at a gas space hourly velocity (GSHV) of 43000 CC h<sup>-1</sup> with 1:1 volume% of CO and O<sub>2</sub> with linear heating rate of 10 °C min<sup>-1</sup>. Gaseous products were analyzed by means of a quadrupole mass spectrometer. For WGS study, 5cc/min CO and 30 cc/min H<sub>2</sub>O vapor were passed along with N<sub>2</sub> over 200 mg of catalyst keeping the total gas flow at 130 cc/min and GSHV of 55900 h<sup>-1</sup>. Gaseous products obtained from the WGS reaction were analyzed by online gas chromatograph (GC). Rate and activation energy of catalyst for CO oxidation and WGS reaction were carried out with different weights (25, 50, 100, 150 to 200 mg) of the catalyst keeping the total flow and GSHV the same.

## 3. Results and discussion

#### (a) Synthesis and characterizations

Only up to 15% Fe ion substituted CeO<sub>2</sub>, Ce<sub>1-x</sub>Fe<sub>x</sub>O<sub>2± $\delta$ </sub> (0  $\leq x \leq$ 0.15) were synthesized by hydrothermal method <sup>30</sup> using NaOH or DETA as precipitating agent. Higher % of Fe<sup>3+</sup> ion substitution and simultaneous substitution of Pd and Fe in ceria could not be achieved by the hydrothermal method. In  $Ce_{1-x}Fe_xO_{2+\delta}$ , (x > 1)0.15) synthesised by the hydrothermal method with DETA or NaOH as a precipitating agent,  $\gamma Fe_2O_3$  impurity phase was precipitated along with  $Ce_{1-x}Fe_xO_{2-\delta}$ .  $Ce_{1-x}Fe_xO_{2-\delta}$  crystallites were not precipitated with DETA or NaOH directly without sonication. Amorphous gel was formed by simultaneous complexation of CAN and Fe(NO<sub>3</sub>)<sub>3</sub>.9H<sub>2</sub>O solutions by DETA. Only after 8 h of sonication, quantitative precipitation of  $Ce_{1-x}Fe_xO_{2-\delta}$  (0  $\leq$  $x \le 0.45$ ) and Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>2- $\delta$ </sub> were obtained. Compounds were brown in color. Even under sonication, precipitation with NaOH instead of DETA results in the formation of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> and  $Ce_{1-x}Fe_xO_{2-\delta}$ . Under hydrothermal condition, the temperature is around 150-200 °C and very high pressure is generated inside the autoclave bombs.<sup>30,31</sup> This facilitates the faster hydrolysis of Fe-DETA complex and Fe<sub>2</sub>O<sub>3</sub> phase is separated out. In the sonochemical method presented here, the temperature reached is 80 °C after 6-8 h of sonication. Thus simultaneous hydrolysis of Ce-DETA and Fe-DETA complexes under sonication results in the precipitation of  $Ce_{1-x}Fe_xO_{2-\delta}$ . Similarly hydrolysis of Ce-DETA, Fe-DETA complex and Pd-DETA complexes under 8 h of sonication results in qualitative precipitation of  $Ce_{1-y-y}Fe_yPd_yO_{2-\delta}$ crystallites.

Powder XRD pattern of as prepared pure CeO<sub>2</sub> and Ce<sub>1-x</sub>Fe<sub>x</sub>O<sub>2- $\delta$ </sub> solid solutions (x = 0.15, 0.25, 0.33 and 0.45) are shown in Fig. 1(a–e) No impurity peaks, corresponding to Ce-DETA complex or Fe-DETA complex or Fe<sub>2</sub>O<sub>3</sub> were observed in powder XRD pattern. All the peaks could be indexed to cubic fluorite and structures were refined by Rietveld method using FullProf program<sup>34</sup> Because of the substitution of smaller Fe<sup>3+</sup> (ionic radii in 8 coordination = 0.78 Å)<sup>35</sup> for Ce<sup>4+</sup> (ionic radii = 0.97 Å)<sup>35</sup> in CeO<sub>2</sub>, systematic decrease in lattice parameter of Ce<sub>1-x</sub>Fe<sub>x</sub>O<sub>2- $\delta$ </sub> (0  $\leq x \leq 0.45$ ) is observed with increasing Fe<sup>3+</sup> ion substitution (Table 1). Decrease in lattice parameter of Ce<sub>1-x</sub>Fe<sub>x</sub>O<sub>2- $\delta$ </sub> (0  $\leq x \leq 0.45$ ) is almost linear with increasing substitution (x) and follows Vegard's law.

Compound	Lattice Parameter ( <i>a</i> )	$\mathbf{R}_{\mathrm{f}}$	$\mathbf{R}_{bragg}$	$\mathbf{R}_{p}$	$\mathbf{R}_{wp}$	R <sub>exp</sub>	$\chi^2$	Crystallite sizes/nm from XRD & (TEM)
CeO <sub>2</sub>	5.413(1)	0.50	0.65	6.32	7.12	6.63	1.14	3.5
$Ce_{0.85}Fe_{0.15}O_{1.925}$	5.384(1)	0.76	1.05	5.23	6.41	5.33	1.43	3.1
$Ce_{0.75}Fe_{0.25}O_{1.875}$	5.346(2)	0.42	0.70	5.50	6.16	5.72	1.15	3.1
$Ce_{0.67}Fe_{0.33}O_{1.835}$	5.339(1)	0.40	0.70	6.08	7.19	6.38	1.27	3.2 (~4)
$Ce_{0.55}Fe_{0.45}O_{1.775}$	5.319(2)	0.86	1.44	7.4	8.9	8.1	1.20	3.1
Ce <sub>0.55</sub> Fe <sub>0.45</sub> O <sub>1.775</sub> heated in air up to 600 °C for 5 h	5.327(2)	0.98	1.38	5.65	7.07	6.67	1.12	4.5
$Ce_{0.67}Fe_{0.33}O_{1.835}$ reduced in H <sub>2</sub> up to 500 °C	5.378(1)	0.37	0.65	5.52	6.80	6.31	1.16	3.6
$Ce_{0.67}Fe_{0.33}O_{1.835}$ heated in air up to 600 °C for 5 h	5.346(1)	0.60	0.89	7.85	9.91	9.13	1.17	3.7
$Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$	5.368(1)	0.21	0.39	5.86	7.02	6.65	1.12	3.1 (~4)
$Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$ $H_2$ reduced up to 450 $^{\circ}C$	5.374(2)	0.56	0.88	6.99	8.47	8.60	0.97	4.2

**Table 1** Structural parameters of  $Ce_{1-x}Fe_xO_{2-\delta}$  (x = 0, 0.15, 0.25, 0.33 and 0.45) and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$ 



**Fig. 1** Powder XRD pattern of  $Ce_{1-x}Fe_xO_{2-x/2}$  (*x* = 0.0, 0.15, 0.25, 0.33 and 0.45) in (a–e) respectively.

We have been able to synthesize up to 45% of Fe<sup>3+</sup> ion substitution in CeO<sub>2</sub> by the sonication method. We have focused our studies on Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>2- $\delta$ </sub> and 2% Pd substituted Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>2- $\delta$ </sub>, Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>2- $\delta$ </sub>. The Rietveld refined powder XRD pattern of Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>2- $\delta$ </sub> is given in Fig. 2(a). The refined X-ray profiles are well fitted with the observed data. Crystallite sizes were estimated by following the Scherrer formula,<sup>36</sup>

Crystallite size 
$$(d) = 0.9\lambda/\beta \cos\theta$$
 (1)

where  $\lambda$  is the wavelength of X-ray,  $\beta$  is the full width at half maxima (FWHM) in radian and  $\theta$  is the diffraction angle. FWHM was estimated by the equation,<sup>37</sup>

$$\beta = (\mathrm{Utan}^2\theta + \mathrm{Vtan}\theta + \mathrm{W})^{1/2}$$
(2)

By taking the U, V, W values from the Rietveld refinement data for (111), (200), (220) and (311) diffraction lines, the crystallite

sizes are found to be in the range of 3 to 5 nm. Crystallite size obtained for  $Ce_{1-x}Fe_xO_{2-\delta}$  from powder XRD data along with lattice parameters,  $R_f$ ,  $R_{bragg}$ ,  $R_p$ ,  $R_{wp}$ ,  $R_{exp}$  and  $\chi^2$  are summarized in Table 1.

Bright field and HRTEM images of  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  are shown in Fig. 3(a, b) Electron diffraction pattern and enlarged view of lattice fringes are shown in the inset of Fig. 3(a, b) respectively. Ring pattern is assigned to fluorite structure and width of lattice fringes are 3.10 Å which agrees well with  $d_{111}$  planes of fluorite lattice (Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>2- $\delta$ </sub>). Absence of diffraction lines and lattice fringes due to Fe<sub>2</sub>O<sub>3</sub> phase suggest that Fe substituted ceria is crystallized to fluorite structure only. Bright field image and HRTEM image also showed that the compound is porous and individual crystallites of 3-4 nm are well interconnected with each other. The SEM image of Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.85</sub> also showed that crystallites are well interconnected and contain pores of 50-100 nm (Fig. 4(a, b)). BET Surface area and porosity measurements of as prepared  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  confirmed that the compound is porous and the surface area and average pore diameter of the compound were found to be 167 m<sup>2</sup> g<sup>-1</sup> and  $\sim$ 2.5 nm respectively (Supporting Figure S1 (a)<sup>†</sup>). Thus  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  crystallites from the sonication method are porous in nature and hierarchically structured with individual crystallites of 3-4 nm.

Thermal stability of materials was studied and the compounds  $(Ce_{1-x}Fe_xO_{2-\delta})$  are found to be stable up to 600 °C in all compositions. Rietveld refined powder XRD profiles of  $Ce_{0.55}Fe_{0.45}O_{2-\delta}$  and  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  heated in air at 600 °C for 10 h are shown in Fig. 2(b, c) Reflections corresponding to any of the Fe<sub>2</sub>O<sub>3</sub> phases are not detected in the XRD patterns. Structural parameters derived from Rietveld analysis are summarized in Table 1. Bright field and HRTEM images of  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  heated at 600 °C for 10 h are shown in Fig. 3(c, d). The compound retained the porous structure and individual crystallites of 6-7 nm are well connected with each other. Electron diffraction pattern and enlarged view of lattice fringes are shown in the insets of Fig. 3(c, d) respectively. The ring pattern is assigned to fluorite structure and the lattice fringes are of 3.11 Å which agrees well with  $d_{111}$  planes of fluorite lattice  $(Ce_{0.67}Fe_{0.33}O_{2-\delta})$ . Absence of diffraction lines and lattice fringes due to any of the Fe<sub>2</sub>O<sub>3</sub> phases suggest that material is stable up to 600 °C. BET Surface area and porosity measurements of as prepared  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  confirmed that the compound is porous and the surface area and average pore diameter of the compound were found to be 53 m<sup>2</sup> g<sup>-1</sup> and  $\sim$ 3.5 nm respectively (Supporting Figure S2 (b)<sup>†</sup>). Further, the SEM image of  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  heated at 600 °C for 10 h also showed that crystallites remain well



Fig. 2 Rietveld refined XRD profile of (a) as prepared  $Ce_{0.67}Fe_{0.33}O_{1.835}$ , (b)  $Ce_{0.55}Fe_{0.45}O_{1.775}$  heated in air at 600 °C for 10 h, (c)  $Ce_{0.67}Fe_{0.33}O_{1.835}$  heated in air at 600 °C for 10 h and (d)  $Ce_{0.67}Fe_{0.33}O_{1.835}$  reduced in H<sub>2</sub> up to 500 °C.

interconnected with microscopic pores of ~50 nm (Fig. 4(c)). Thus the hierarchical structure of the compound remains stable even after sintering at 600  $^{\circ}$ C for 10 h.

Substitution of Fe<sup>3+</sup> ion in CeO<sub>2</sub> was also examined by UV-visible spectroscopy. UV-visible spectra of (a)  $CeO_2$ , (b)  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  (as prepared), (c)  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  heated at 550 °C for 48 h, (d)  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  heated at 800 °C for 5 h and (e)  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> are shown in Fig. 5.  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (curve e) shows three distinct bands near to 865 nm, 661 nm and 540 nm. CeO<sub>2</sub> made by the same sonication method showed a strong absorption band near 358 nm and adsorption edge near to 462 nm.<sup>30</sup> UV-visible absorption of  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  (curve b) shows a broad absorption with band edge at 801 nm and no distinct peaks were seen due to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>. On heating at 550 °C for 48 h also, there were no change in spectra (curve c) and an absorption edge was observed at 750 nm. Since  $Fe^{3+}$  is substituted in fluorite lattice, distinct  $Fe_2O_3$  type absorption bands were not observed, only broad absorption is observed.<sup>38</sup> UV-visible spectra of  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  heated at 800 °C for 5 h (curve d) showed distinct absorption bands near 876 nm, 669 nm, 531 nm similar to  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> (curve e). This because Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>2- $\delta$ </sub> is stable up to 600 °C only, when heated at above 600 °C (800 °C in this case) it decomposes to  $Ce_{1-x}Fe_xO_{2-\delta} + \gamma Fe_2O_3$ . That is why the UV-visible spectra of  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  heated at 800 °C contain the absorption band for y-Fe<sub>2</sub>O<sub>3</sub>. Thus UV-visible spectra

of  $Ce_{_{0.67}}Fe_{_{0.33}}O_{_{2-\delta}}$  samples also confirm  $Fe^{^{3+}}$  ion substitution in the  $CeO_2$  lattice.

Rietveld refined powder XRD pattern of  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  is shown in Fig. 6(a) All the diffraction peaks could be indexed to fluorite structure only and no impurity peaks or residual intensities are observed corresponding to Pd metal or PdO in the Rietveld refined XRD pattern. Bright field and HRTEM images of  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  are shown in Fig. 3(e, f) Crystallites are porous structured with individual crystallites of 3-4 nm, which is close to the sizes obtained from the Rietveld refined XRD data (Table 1). The inset of Fig. 3(e) shows the ring type diffraction pattern and the inset of Fig. 3(f) shows an enlarged view of the lattice fringes of  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$ . The electron diffraction pattern was indexed to fluorite structure and lattice fringes of 3.11 Å corresponding to  $d_{111}$  of fluorite Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>2- $\delta$ </sub>. Absence of diffraction rings and lattice fringes, corresponding to Fe<sub>2</sub>O<sub>3</sub> and PdO or Pd suggest that Fe and Pd are substituted in CeO<sub>2</sub>. EDX study has been carried out over the lattice fringes (111 planes) of nanocrystallites by the EDX probe in the TEM instrument (Fig. 3(g)) and indeed Ce, Fe and Pd were found in the ratio of 0.65 : 0.32 : 0.03, which agrees well with the composition taken for the preparation. BET surface area and porosity measurements of as prepared  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  showed that surface area and average pore diameter of the compound are



**Fig. 3** (a) Bright field image and (b) HRTEM image of  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  and indexed electron diffraction pattern and enlarged view of lattice fringes in the inset of (a, b) respectively. (c) Bright field image and (d) HRTEM image of  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  heated at 600 °C for 10 h and indexed electron diffraction pattern and enlarged view of lattice fringes in the inset of (c, d) respectively. (e) Bright field and (f) HRTEM image of  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  and indexed electron diffraction pattern and enlarged view of lattice fringes in the inset of (c, d) respectively. (e) Bright field and (f) HRTEM image of  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  and indexed electron diffraction pattern and enlarged view of lattice fringes in the inset of (e, f) respectively. (g) EDX analysis pot of  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  nanocrystallites.

169 m<sup>2</sup> g<sup>-1</sup> and ~3 nm respectively (Supporting Figure S1(c)†). The SEM image of as prepared Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>2- $\delta$ </sub> also showed that the crystallites are interconnected and contain microscopic pores of 50–100 nm (Fig. 4(d)). Thus TEM, SEM and BET surface area and porosity measurements confirmed that the compound is porous and hierarchically structured with individual crystallites of 3–4 nm.

The electronic structure of  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$ and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  were investigated by X-ray photo-electron spectroscopy. Core level Fe(2p) spectra of  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  are shown in Fig. 7(a, b) In both cases binding energy of  $Fe(2p_{3/2})$  is observed at 710.4 eV and a weak satellite at 8 eV from the main peak confirms that Fe is in +3state.<sup>39</sup> Ce(3d) spectra of  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$ are shown in Fig. 8(a, b). Ce  $(3d_{5/2})$  peak was observed at 882.7 eV along with satellite peaks at 6.4 and 16 eV from the main peak, which are the characteristic peaks of Ce4+ in CeO2.40 Thus Ce is in +4 state in  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$ . Core level Pd(3d) spectrum of  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  is shown in Fig. 9(a).  $Pd(3d_{5/2})$  binding energy is observed at 337.6 eV, which is higher than the binding energy of  $Pd^{2+}(3d_{5/2})$  in  $PdO^{41}$  but lower than the binding energy of  $Pd^{2+}(3d_{5/2})$  in  $PdCl_2^{19}$  So Pd is in +2 state in  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$ . Accordingly formulae of the compounds can be written as  $Ce_{0.67}Fe_{0.33}O_{1.835}$  and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$ .

An estimate of relative concentrations of Ce and Fe and Ce : Fe : Pd were carried out from the intensities of Fe(2p) and Ce(3d) and Pd (3d) peaks in  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$ . Relative surface concentration is calculated from the formula:<sup>42</sup>

Relative concentration 
$$C_{\rm M} = (I_{\rm M}/\lambda_{\rm M}.\sigma_{\rm M}.D_{\rm M})/\Sigma(I_{\rm M}/\lambda_{\rm M}.\sigma_{\rm M}.D_{\rm M})$$
 (3)

where  $I_{\rm M}$  is the integrated intensity of the core levels (M = Ce(3d), Fe(2p) and Pd (3d)),  $\lambda_{\rm M}$  is the mean escape depth of the respective photoelectrons,  $\sigma_{\rm M}$  is the photoionization cross section, and  $D_{\rm M}$  is the geometric factor. The photoionization cross-section values were taken from Scofield's data<sup>43</sup> and mean escape depths were taken from Penn's data.<sup>44</sup> The geometric factor was taken as 1, because the maximum intensity in this spectrometer is obtained at 90°. Surface concentrations of Ce and Fe are found in the ratio of 0.68:0.32 in Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>2-\delta</sub> and surface concentrations of Ce, Fe and Pd were found in the ratio of 0.67: 0.30:0.03 in Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>2-\delta</sub>. Thus surface compositions of Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>2-\delta</sub> and Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>2-\delta</sub>.

## (b) OSC

Redox properties or OSC of  $Ce_{1-x}Fe_xO_{2-\delta}$  and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$ were studied by H<sub>2</sub>/TPR or hydrogen uptake. Hydrogen uptake measurements were performed repeatedly by reducing the compound in H<sub>2</sub> up to 550 °C followed by oxidation in O<sub>2</sub> at 350 °C. H<sub>2</sub>/TPR plots of Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>2- $\delta$ </sub> for 6 consecutive cycles are given in Fig. 10(a-f) and OSC is fully reversible. OSC of all compositions of  $Ce_{1-x}Fe_xO_{2-\delta}$  are given in Table 2 and increase with increase in Fe substitution.  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  releases ~0.31 [O]/mole of compound or OSC equivalent to 2205 µmol of [O]/g. OSC of Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>2-δ</sub> heated at 600 °C for 10 h was also studied and OSC was found to ~0.3 [O]/mole of compound (Fig. 10(g)). Maximum OSC expected for Ce<sub>0.5</sub>Zr<sub>0.5</sub>O<sub>2</sub> is 0.25 mol of [O]/mol or 1693 µmol g<sup>-1</sup> and the highest OSC realized experimentally for  $Ce_{0.5}Zr_{0.5}O_2$  up to 600 °C is 0.22 mol of [O]/mol or 1500  $\mu$ mol g<sup>-1</sup>.<sup>22</sup> The high OSC (0.31 [O]/mole) of  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  suggests that  $Ce_{0.67}{}^{4+}Fe_{0.33}{}^{3+}O_{1.835}$  is reduced to  $Ce_{0.38}{}^{4+}Ce_{0.29}{}^{3+}Fe_{0.33}{}^{2+}O_{1.525}$  state. OSC of  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub> synthesized by solution combustion method<sup>45</sup> was also studied and OSC plot of yFe2O3 equivalent to amount of Fe<sup>3+</sup> ions present in Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>2- $\delta$ </sub> was given in Fig. 10(a) Fe<sub>2</sub>O<sub>3</sub> is reduced to Fe<sub>2</sub>O<sub>2.65</sub> state up to 600 °C. It means not all Fe<sup>3+</sup> is reduced  $Fe^{2+}$  state in  $Fe_2O_3$  whereas in  $Ce_{1-x}Fe_xO_{2-\delta}$ , all  $Fe^{3+}$  ions



Fig. 4 (a, b) SEM images of as prepared  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$ , (c) SEM image of  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  heated at 600 °C for 10 h and (d) SEM images of as prepared  $Ce_{0.67}Fe_{0.33}Pd_{0.02}O_{2-\delta}$ .



Fig. 5 UV-visible spectra of (a) CeO<sub>2</sub>, (b) as prepared Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>2- $\delta$ </sub>, (c) Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>2- $\delta$ </sub> heated at 500 °C, (d) Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>2- $\delta$ </sub> heated at 800 °C and (e)  $\gamma$ -Fe<sub>2</sub>O<sub>3</sub>.

are reduced to  $Fe^{2\scriptscriptstyle +}$  state along with partial reduction of  $Ce^{4\scriptscriptstyle +}$  to  $Ce^{3\scriptscriptstyle +}$  state.

Electronic states of H<sub>2</sub> reduced sample (Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.525</sub>) were examined by X-ray photo-electron spectroscopy. Core level Fe(2p) spectrum of reduced sample is shown in Fig. 7(c). Fe(2p) binding energy is observed at 709.9 eV and an almost negligible satellite peak 8 eV from the main peak confirms that Fe is in +2 state.<sup>39</sup> Ce(3d) core level spectrum is shown in Fig. 8(c). The Ce<sup>4+</sup>( $3d_{5/2}$ ) peak observed at 882.7 eV along with satellite peaks at 6.4 and 16 eV below the main peak are characteristic of Ce<sup>4+</sup> in CeO<sub>2</sub>.<sup>40</sup>  $Ce^{3+}(3d_{5/2})$  in  $Ce_2O_3$  is characterized by  $Ce(3d_{5/2})$  at 883.3 eV along with an intense satellite at 887.1 eV.40 Thus filling of the valley between Ce4+(3d5/2) at 882.7 eV and its satellite at 889.1 eV (Fig. 8(c)) confirmed that Ce is in a mixed valence (+4 and +3) state in  $H_2$  reduced  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$ . Thus XPS of Ce(3d) and Fe(2p) also confirmed that both Fe<sup>3+</sup> and Ce<sup>4+</sup> were reduced in H<sub>2</sub> uptake experiments at such a low temperature (~400 °C). Rietveld refined powder XRD pattern of H<sub>2</sub> reduced Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.835</sub> viz Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.525</sub> is shown in Fig. 2(d). FeO or Fe<sub>2</sub>O<sub>3</sub> is not separated out during  $H_2$  reduction. Due to the presence of  $Fe^{2+}$  and  $Ce^{3+}$ state in H<sub>2</sub> reduced sample, an increase in lattice parameter of  $Ce_{0.67}Fe_{0.33}O_{1.525}$  (a = 5.378 Å) is observed compared to as prepared  $Ce_{0.67}Fe_{0.33}O_{1.835}$  (*a* = 5.339 Å).

2-0

Compound	Composition		
	Before H <sub>2</sub> reduction	After H <sub>2</sub> reduction	OSC/µmol g <sup>-1</sup> up to 550 °C
CeO <sub>2</sub>	$Ce^{4+}O_2$	$Ce^{4+}_{0.74}Ce^{3+}_{0.26}O_{187}$	745
$Ce_{0.85}Fe_{0.15}O_{1.925}$	$Ce_{0.85}^{4+}Fe_{0.15}^{3+}O_{1.925}$	$Ce^{4+}_{0.59}Ce^{3+}_{0.26}Fe^{2+}_{0.15}O_{1.71}$	1353
$Ce_{0.75}Fe_{0.25}O_{1.875}$	$Ce_{0.75}^{4+}Fe_{0.25}^{3+}O_{1.875}$	$Ce_{0.45}^{4+}Ce_{0.30}^{3+}Fe_{0.25}^{2+}O_{1.595}$	1883
$Ce_{0.67}Fe_{0.33}O_{1.835}$	$Ce_{0.67}^{4+}Fe_{0.33}^{3+}O_{1.835}$	$Ce_{0.38}^{4+}Ce_{0.29}^{3+}Fe_{0.33}^{2+}O_{1.525}$	2205
$Ce_{0.55}Fe_{0.45}O_{1.775}$	$Ce_{0.55}^{4+}Fe_{0.45}^{3+}O_{1.775}$	$Ce^{4+}_{0.40}Ce^{3+}_{0.15}Fe^{2+}_{0.45}O_{1.475}$	2286
$Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$	$Ce_{0.65}{}^{4+}Fe_{0.33}{}^{3+}Pd^{2+}{}_{0.02}O_{1.815}$	$Ce^{4+}{}_{0.26}Ce^{3+}{}_{0.39}Fe^{3+}{}_{0.33}Pd_{0.02}O_{1.60}$	1526 up to 200 °C



**Fig. 6** Rietveld refined Powder XRD pattern of  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  (a) as prepared and (b) reduced in H<sub>2</sub> up to 500 °C.

Reversibility of OSC of  $Ce_{0.67}Fe_{0.33}O_{1.835}$  can be explained on the basis of redox potentials of  $Fe^{3+}/Fe^{2+}(0.77 \text{ V})$  and  $Ce^{4+}/Ce^{3+}(1.61 \text{ V})$ . In general transition metal ion substituted  $CeO_2$  are reduced at a lower temperature than pure  $CeO_2$ . Preferential absorption of  $H_2$  or CO on transition metal ions seems to be the reason for this.<sup>20,28,30</sup> Thus in the presence of  $H_2$ , due to preferential adsorption of hydrogen on  $Fe^{3+}$ , first  $Fe^{3+}$  will be reduced to  $Fe^{2+}$  and due to lower redox potentials of  $Fe^{3+}/Fe^{2+}$ than the redox potentials of  $Ce^{4+}/Ce^{3+}$  the following redox reaction occurs:

$$Fe^{2+} + Ce^{4+} \rightarrow Fe^{3+} + Ce^{3+}$$
 (4)

The reduced Ce<sup>3+</sup> is oxidized by feed oxygen:



**Fig. 7** Core level Fe(2p) spectra in (a) as prepared  $Ce_{0.67}F_{0.33}O_{2-\delta}$ , (b) as prepared  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$ , (c)  $Ce_{0.67}F_{0.33}O_{2-\delta}$  reduced in hydrogen up to 500 °C, (d)  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  reduced in hydrogen up to 500 °C and (e)  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  after chronoamperometry experiment at 1.2 V.

$$2Ce^{3+} + O_2 \rightarrow 2Ce^{4+} + O^{2-}$$
 (5)

So redox couples play a crucial role in reversible OSC of  $Ce_{0.67}Fe_{0.33}O_{1.835}$ .

Having studied the reversible OSC of  $Ce_{0.67}Fe_{0.33}O_{1.835}$ , OSC of  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  was also studied by H<sub>2</sub>/TPR to see the effect of Pd<sup>2+</sup> ion substitution on OSC. H<sub>2</sub>/TPR plot of  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  is shown in Fig. 11(a) and plots for same amount of CeO<sub>2</sub> and Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.835</sub> are also given in Fig. 11(b, c) respectively for comparison. Interestingly a single sharp hydrogen uptake occurs below 150 °C with a reduction peak at 125 °C. Hydrogen uptake of the material, Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub> heated at 600 °C for 24 h was also studied and there was no decrease in OSC except the sharp reduction peak is shifted to 165 °C from 125 °C (Supporting Figure S2†). OSC of Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub> is found 1526 µmol g<sup>-1</sup> up to 200 °C or equivalent to release of 0.215 [O]/mol of compound. H/Pd ratio is found to be as high as 21.5. Ideally it should be equal to 2 if Pd<sup>2+</sup> is reduced to Pd<sup>o</sup>. This higher H/Pd ratio suggests hydrogen spill-over from Pd<sup>2+</sup> ion to



**Fig. 8** Core level Ce(3d) spectra in (a) as prepared Ce<sub>0.67</sub>F<sub>0.33</sub>O<sub>2- $\delta$ </sub>, (b) as prepared Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>2- $\delta$ </sub>, (c) Ce<sub>0.67</sub>F<sub>0.33</sub>O<sub>2- $\delta$ </sub> reduced in hydrogen up to 500 °C, (d) Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>2- $\delta$ </sub> reduced in hydrogen up to 500 °C and (e) Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>2- $\delta$ </sub> after chronoamperometry experiment at 1.2 V.



**Fig. 9** XPS of Pd(3d) core level in  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  (a) as prepared, (b) reduced in hydrogen up to 500 °C and (c) after chronoamperometry experiment at 1.2 V.



Fig. 10  $(a-f) H_2/TPR$  or hydrogen uptake profile of  $Ce_{0.67}Fe_{0.33}O_{1.835}$  for 6 consecutive cycles and (g) hydrogen uptake of  $Ce_{0.67}Fe_{0.33}O_{1.835}$  heated at 600 °C for 24 h.  $H_2/TPR$  of equivalent mol of  $Fe_2O_3$  is also given in (a) for comparison.



Fig. 11  $H_2/TPR$  or hydrogen uptake profile of (a)  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$ , (b)  $CeO_2$  and (c)  $Ce_{0.67}Fe_{0.33}O_{1.835}$ .

neighboring Fe<sup>3+</sup> and Ce<sup>4+</sup> ions in Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub>. Though Fe<sup>3+</sup> and Ce<sup>4+</sup> reduction occurs at ~400 °C in Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.835</sub>, no separate reduction peak is observed for Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub> up to 500 °C. This clearly indicates Fe<sup>3+</sup> and Ce<sup>4+</sup> ions are also reduced along with Pd<sup>2+</sup> ions in Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub>. Thus Pd<sup>2+</sup> ion substitution in Ce<sub>1-x</sub>Fe<sub>x</sub>O<sub>2-δ</sub> induces the synergistic effect by bringing down the H<sub>2</sub> reduction temperature of Ce<sup>4+</sup> and Fe<sup>3+</sup> ions.

Hydrogen reduced  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  *i.e.*  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.6}$  was black in color but as soon it was exposed to air, it became hot and regained the original brown color suggesting that the compound is oxidized in air. Therefore XRD and XPS of the

hydrogen reduced samples were recorded by first cooling it by liquid N<sub>2</sub> followed by covering the surface with liquid paraffin to avoid air oxidation as much as possible. Rietveld refined powder XRD pattern of H<sub>2</sub> reduced Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub> up to 500 °C is shown in Fig. 6(b) and impurity peaks corresponding to Pd metal, PdO, Fe metal or FeO<sub>x</sub> were not observed. An increase in lattice parameter of H<sub>2</sub> reduced Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub> viz  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.60}$  (a = 5.374 Å) was observed compared to as prepared  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  (*a* = 5.368 Å). Core level Pd (3d) spectrum of the H<sub>2</sub> reduced sample is shown in Fig. 9(b) and is resolved into Pd<sup> $\circ$ </sup> and Pd<sup>2+</sup> states. Binding energy for Pd<sup> $\circ$ </sup>(3d<sub>5/2</sub>) is observed at 335.1 eV19 and binding energy for Pd2+(3d5/2) was observed at 337.2 eV. Thus Pd is present in mixed valence 0 and +2 states in the ratio of 35:65 in the H<sub>2</sub> reduced sample. Core level Fe(2p) spectrum of the reduced sample is shown in Fig. 7(d). The Fe(2p) main peak is observed at 710.4 eV and a satellite peak 8 eV from the main peak confirms that Fe was in 3+ state. Ce(3d) core level spectrum is shown in Fig. 8(d) and cerium ion was present in mixed valance +3 and +4 oxidation states.

Hydrogen uptake measurements were performed repeatedly by reducing in H<sub>2</sub> up to 200 °C and oxidizing in O<sub>2</sub> at 50 °C and found to be fully reversible. Hydrogen uptake for five consecutive cycles are shown in Fig. 12(a–e). Reversible OSC of Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub> can be explained on the basis of redox potentials of Pd<sup>2+/0</sup>(0.89 V), Fe<sup>3+/2+</sup>(0.77 V) and Ce<sup>4+/3+</sup>(1.61 V). Due to the lower reduction potential of Fe<sup>3+/2+</sup> compared to Pd<sup>2+/0</sup> and Ce<sup>4+/3+</sup>, it is prone to faster oxidation and Pd can act as bridge between Fe and Ce in terms of fast electron transfer; the redox reaction can be written as:

$$2Fe^{2+} + Pd^{2+} \to 2Fe^{3+} + Pd^{\circ}$$
(6)

$$Pd^{0} + 2Ce^{4+} \rightarrow Pd^{2+} + 2Ce^{3+}$$
 (7)

and Ce<sup>3+</sup> is further oxidized by feed oxygen

$$2Ce^{3+} + O_2 \to 2Ce^{4+} + O^{2-}$$
 (8)

The absence of  $Fe^{2+}$  in  $H_2$  reduced sample (Fig. 6(d)) also suggests that Pd ion is enhancing or accelerating the electron transfer from  $Fe^{2+}$  to  $Ce^{4+}$  and that is why the compound also gets hot when



Fig. 12 Hydrogen uptake of  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  for five consecutive cycles in (a–e).

exposed to air due to fast oxidation of  $Fe^{2+}$  to  $Fe^{3+}$ . Thus due to synergistic interaction of redox couples of  $Pd^{2+/0}(0.89 \text{ V})$  with  $Fe^{3+/2+}(0.77 \text{ V})$  and  $Ce^{4+/3+}(1.61 \text{ V})$ , such a high OSC was observed at lower temperature in  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$ .

Further to observe the synergistic redox interaction of Pd<sup>2+/0</sup>(0.89 V), Fe<sup>3+/2+</sup>(0.77 V) and Ce<sup>4+/3+</sup>(1.61 V) redox couples in Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.835</sub> and Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub>, electrochemical O<sub>2</sub> evolution experiments were carried out with Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.835</sub> and Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub> electrodes. Electrochemical O<sub>2</sub> evolution was studied by cyclovoltammetry and chronoamperometry experiments in 0.5 M H<sub>2</sub>SO<sub>4</sub> using Pt as counter electrode and saturated calomel electrode (SCE) as a reference electrode. A working electrode was made by mixing a known amount of catalyst with 45 wt% of graphitic carbon and 5 wt% of PVDF (polyvinyledenedifluoride) binder followed by depositing a thin layer of this slurry on a graphite paper over an area of 1 cm<sup>2</sup>. The cyclic voltammograms for CeO\_2, Ce\_{0.98}Pd\_{0.02}O\_{2-\delta}, Ce\_{0.67}Fe\_{0.33}O\_{1.835} and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  in 0.5 M H<sub>2</sub>SO<sub>4</sub> from 0.0 V to 1.2 V are shown in Fig. 13(a-d). Ce4+ reduction starts over ~1 V in pure CeO2. In the case of  $Ce_{0.98}Pd_{0.02}O_{2-\delta}$  a reduction peak is observed at ~0.8 V, in the case of  $Ce_{0.67}Fe_{0.33}O_{1.835}$  and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  a reduction peak is observed at ~0.7 V. No separate reduction peak is observed with  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  electrode suggesting that reduction of  $Pd^{2+}$ , Fe<sup>3+</sup> and Ce<sup>4+</sup> is occurring simultaneously which is also reflected in terms of a higher current for the  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  electrode compared to Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>2-\delta</sub>, Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.835</sub> and CeO<sub>2</sub>. Further higher electro-oxidation or higher O2 evolution is confirmed by chronoamperometry. Chronoamperometry plots of oxygen evolution at 1.2 V for CeO<sub>2</sub> (a), Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>2- $\delta$ </sub> (b), Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.835</sub> (c) and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  (d) in 0.5 M H<sub>2</sub>SO<sub>4</sub> solution are shown in the inset of Fig. 13. Higher current density is observed with Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub> compared to the same amount of CeO<sub>2</sub>, Ce<sub>0.98</sub>Pd<sub>0.02</sub>O<sub>2- $\delta$ </sub> and Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.835</sub>. So similar to H<sub>2</sub> uptake measurements (H/Pd = 21.5 for  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$ ), much higher current density in electrochemical  $O_2$  evolution for Ce0.65Fe0.33Pd0.02O1.815 electrode is observed compared to other  $CeO_2$ ,  $Ce_{0.98}Pd_{0.02}O_{2-\delta}$  and  $Ce_{0.67}Fe_{0.33}O_{1.835}$  electrodes. Thus the



Fig. 13 Cyclic voltammogram for oxygen evolution with (a) CeO<sub>2</sub>, (b)  $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ , (c)  $Ce_{0.67}Fe_{0.33}O_{1.835}$  and (d)  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  and, in inset, chronoamperometry plot with (a)  $CeO_2$ , (b)  $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ , (c)  $Ce_{0.67}Fe_{0.33}O_{1.835}$  and (d)  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  in 0.5 M H<sub>2</sub>SO<sub>4</sub>.

absence of separate reduction peaks for  $Fe^{3+}$  and  $Pd^{2+}$  in the cyclic voltammogram and highest current density for  $O_2$  evolution with  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  electrode can be attributed to synergistic interaction of  $Pd^{2+/0}$  redox couples with  $Fe^{3+/2+}$  and  $Ce^{4+/3+}$  redox couples in  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$ . Oxygen evolution reaction with  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  electrode can be written as

$$Ce^{4+}{}_{0.65}Fe^{3+}{}_{0.33}Pd^{2+}{}_{0.02}O_{1.815} + H_2O \Leftrightarrow Ce^{4+/3+}{}_{0.65}Fe^{3+/2+}{}_{0.33}Pd^{2+/0}{}_{0.02}O_{1.815-z} + 2H^+ + 2\bar{e} + 1/2(1+z)O_2 \quad (9)$$

$$(z \sim 0.2)$$

Once the steady state with z = 0.2 is reached, further O<sub>2</sub> evolution occurs due to the water splitting:

$$2H_2O \rightarrow O_2 + 4H^+ + 4e^-$$
 (10)

To observe the high reducibility of Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub>, electronic states of Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub> electrode after chronoamperometry experiment at 1.2 V were examined by X-ray photo-electron spectroscopy. The electrodes were taken out from the electrochemical cell, dried at 60 °C in a hot air oven and mounted directly inside the X-ray photo-electron spectroscopy chamber. The core level Fe(2p) spectrum shown in Fig. 7(e) indicates the presence of Fe in a mixed valence (+2/+3) state. Ce(3d) core level spectrum is shown in Fig. 8(e) and Ce was also present in mixed a valence (+3/+4) state. Pd(3d) core level spectrum is shown in Fig. 9(c) and Pd is present in both +2 and 0 oxidation states. Since the catalyst was coated with graphite powder and deposited on graphite paper and binder coating, the electrochemically reduced oxide remained in a reduced state even on exposure to air. Thus XPS study also confirms the higher reducibility of  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  electrode in electrochemical oxygen evolution.

#### (c) CO oxidation

To see the applicability of high OSC in exhaust catalysis, CO oxidations were carried out with the catalysts both in the presence of external oxygen and direct utilization of lattice oxygen was also studied by CO oxidation in absence of feed oxygen. %CO conversions both in the presence and in the absence of feed oxygen over  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  and  $Ce_{0.67}Fe_{0.33}O_{1.835}$  are shown in Fig. 14(a). Complete conversion of CO to CO<sub>2</sub> was achieved below 85 °C with  $Ce_{\scriptscriptstyle 0.65}Fe_{\scriptscriptstyle 0.33}Pd_{\scriptscriptstyle 0.02}O_{\scriptscriptstyle 1.815}$  and below 250 °C with Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.835</sub> in the presence of feed oxygen. Utilization of lattice oxygen was shown with both catalysts for CO oxidation in the absence of feed oxygen. In the case of Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.835</sub>, CO conversion in the absence of feed oxygen is observed in a broad temperature range (150 to 550 °C) and it increases with increasing temperature suggesting that lattice oxygen is activated by Fe ion substitution in ceria. The amount of lattice oxygen utilized for CO oxidation is also calculated by taking the area under the CO oxidation plot and the amount of lattice oxygen utilized directly by CO was found to 0.31 [O]/mol of compound which is in close agreement with the OSC observed by  $H_2/TPR$ . In the case of Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub>, high CO conversion is observed in a narrow temperature range (30-150 °C) with a reduction peak around 90  $^{\circ}\mathrm{C}.$  The area under the reduction peak is also calculated and the amount of lattice oxygen utilized for CO oxidation was found to be 0.23 [O]/mol of compound which is almost equal to the OSC of compound observed by  $H_2/TPR$ . Thus feed  $O_2$  can be reversibly exchanged with lattice oxygen in Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.835</sub> and Ce0.65 Fe0.33 Pd0.02 O1.815 for CO oxidation.



**Fig. 14** (a) CO oxidation with  $Ce_{0.67}Fe_{0.33}O_{1.835}$  and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$ both in presence and absence of O<sub>2</sub>, (b) % CO conversion *vs.* W/F with  $Ce_{0.65}Fe_{0.22}Pd_{0.02}O_{1.815}$  at different temperatures and (c) rate (R) *vs.* temperature plot and Arrhenius plot (Ln(r) *vs.* 1000/*T*/K in the inset of (c).

Keeping the flow rate and GSHV same, CO oxidation was also carried out with different weights of the catalysts to obtained the actual rates from the equation,

 Table 3
 Rate and activation energies for CO oxidation and wgs reaction with different catalysts

Reaction	Catalyst	Rate/ $\mu$ mol g <sup>-1</sup> s <sup>-1</sup> ( $T/^{\circ}$ C)	Ea/kJ mol <sup>-1</sup>	Reference
$CO + O_2$	5 wt% Ru/SiO <sub>2</sub>	1.00 (110)	94	9
	$5 \text{ wt\% Pd/SiO}_2$	0.316 (143)	103	9
	5 wt% Pt/SiO <sub>2</sub>	0.32 (115)	56	9
	$Ce_{0.98}Pd_{0.02}O_{1.98}$	3.9 (120) 0 57(100)	121	25
$Ce_{0.95}F$ $Ce_{0.90}F$ $Ce_{0.73}T$	$Ce_{0.95}Ru_{0.05}O_{1.97}$	2.05(100)	92.2	21
	$Ce_{0.90}Ru_{0.10}O_{1.94}$	3.3(100)	43	21
	$Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}$	· · /	53.5	17
	$Ce_{0.83}Sn_{0.15}Pd_{0.02}O_{2-\delta}$		82.4	19
Ce <sub>0.65</sub>	$Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$	4.1(80)	38.0	Present study

$$Rate(\mathbf{R}) = (F/W).x \tag{11}$$

where F is flow of gaseous molecules in mole s<sup>-1</sup>, W is the weight of the catalyst (g) and x is fractional conversion. Fractional conversion with W/F was plotted at different temperatures as shown in Fig. 14(b) for  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$ . The weight of the catalysts, W, were varied from 25 to 200 mg, whereas F, the flow rate (mol s<sup>-1</sup>), was kept constant. The plot is linear up to nearly 70% conversion, and the reaction rates at different temperatures determined from the slopes of the linear region are shown in Fig. 14(c). The Arrhenius plot is also shown in the inset of Fig. 14(c). Activation energy was also calculated from the rates derived from W/F plots and it is equal to 38 kJ mol<sup>-1</sup>. A comparison of rate and activation energy with different catalyst for CO oxidation is given Table 3.  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  is found superior to the other noble metal ion substituted and metal impregnated catalysts.<sup>9,17,19,21,25</sup>

## (d) WGS reaction

The WGS reaction is an important reaction which produces  $H_2$  from oxidation of CO with water and the reaction is written as:

$$CO + H_2O \to CO_2 + H_2 (\Delta H = -41.1 \text{ kJ mol}^{-1}, \Delta G = -28.6 \text{ kJ mol}^{-1})$$
(12)

Essentially the WGS reaction is a two step reaction, the first step involves oxidation CO by utilizing the lattice oxygen of the catalyst and in the second step catalyst is regenerated by  $H_2O$  releasing  $H_2$ . Since  $Ce_{0.67}Fe_{0.33}O_{1.835}$  and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$ showed high OSC both by H<sub>2</sub>/TPR and by CO oxidation in absence of external oxygen they can be good catalysts for H<sub>2</sub> production via WGS reaction. Therefore WGS reactions were studied with these catalysts. In the product stream, volumes of CO, CO<sub>2</sub> and H<sub>2</sub> were measured independently in GC and CO<sub>2</sub> formation (CO oxidation to CO<sub>2</sub> by H<sub>2</sub>O), H<sub>2</sub> formation and CO consumption plots with Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub> catalyst are shown in Fig. 15(a). % CO conversion was over 97% at ≥375 °C. Possible by-products of the reaction such as CH<sub>3</sub>OH, H<sub>2</sub>CO, CH<sub>4</sub>, and other hydrocarbons were not detected in the product stream in the detection limit of 3-5 ppm. CO conversion is almost 100% H<sub>2</sub> specific over this catalyst. % CO conversion profiles with CeO<sub>2</sub>, Ce<sub>0.85</sub>Fe<sub>0.15</sub>O<sub>1.925</sub>, Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.835</sub> and Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub> are shown in Fig. 15(b-e) respectively for comparison. Practically no conversion observed with pure CeO<sub>2</sub>, almost 10% CO conversion to CO2 with equivalent amount of H2 production was observed at 375 °C with Ce<sub>0.85</sub>Fe<sub>0.15</sub>O<sub>1.925</sub> and ~74% conversion



Fig. 15 (a) % CO consumption,  $CO_2$  and  $H_2$  formation plots with  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$ , % CO conversion to  $CO_2$  by  $H_2O$  vapors with  $CeO_2$ ,  $Ce_{0.85}Fe_{0.15}O_{1.925}$ ,  $Ce_{0.67}Fe_{0.33}O_{1.835}$  and  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  in (b–e) respectively. (f) % CO conversion,  $H_2$  and  $CO_2$  formation plots with  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$  in presence for externally fed  $H_2$  and  $CO_2$ .

was achieved at 375 °C and almost 98% conversion was achieved at 480 °C with Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.835</sub>. Thus with increasing Fe<sup>3+</sup> ion substitution in CeO<sub>2</sub>, higher WGS activity (CO conversion to CO<sub>2</sub> by water) was observed which suggests that higher OSC is beneficial for high conversion in WGS reaction. About 97% conversion of CO to CO<sub>2</sub> and equivalent H<sub>2</sub> production was observed at 375 °C with Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.835</sub>. Since WGS is an exothermic reaction, complete (100%) conversion is not reached and equilibrium conversion is reached to 97% only with these catalysts at high temperature (≥375 °C). Activation energy for  $CO + H_2O \rightarrow CO_2 + H_2$  were estimated from the rates for <15%conversion by using Arrhenius' equation. Activation energies are found to be 52.1 and 61.3 kJ mol<sup>-1</sup> for  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{1.815}$ and Ce<sub>0.67</sub>Fe<sub>0.33</sub>O<sub>1.835</sub> catalysts respectively. To get the actual rate and activation energy of catalyst (Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub>), WGS reactions were carried out with different weights (25, 50, 100, 150 to 200 mg) of the catalyst, keeping the total flow and GSHV the same. Fractional conversion vs. W/F plot is given in Fig. 16(a). Rates (R) were derived from slopes of the plot Fig. 16(a) and rate vs.  $T/^{\circ}$ C is given in Fig. 16(b). Ln(R) vs. 1000(T/K) is given in the inset of Fig. 16(b) The rate was found to be as high as 27.2  $\mu$ mol g<sup>-1</sup> s<sup>-1</sup> at 375 °C and activation energy was found to be 46.4 kJ mol<sup>-1</sup>. To see the viability of the catalyst, WGS reaction was also studied in the presence of externally fed H<sub>2</sub> and CO<sub>2</sub> with a gas mixture flow (CO (5 cc/min),  $CO_2$  (10cc/min) and  $H_2$ (10 cc/min balance in  $N_2$ ) keeping total gas flow and GSHV the same with 200 mg of catalyst. Up to 35% CO conversion to CO<sub>2</sub>



**Fig. 16** (a) Fraction conversion of CO to CO<sub>2</sub> by  $H_2O \nu s$ . W/F plot with 25, 50, 100, 150 and 200 mg of Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub> for WGS reaction. (b) Rate (R)  $\nu s$ . temperature plot and Arrhenius plot (Ln(R))  $\nu s$ . 1000/*T*/K in the inset of (b).

was observed at ~275 °C and almost 98% conversion observed at 500 °C with 100% H<sub>2</sub> selectivity (Fig. 15(f)). Up to 600 °C, no trace of byproducts of the reaction such as methane, hydrocarbons, CH<sub>3</sub>OH and H<sub>2</sub>CO were detected in the product stream in the detection limit of 3–5 ppm. Thus even in presence of a large amount of externally fed H<sub>2</sub> and CO<sub>2</sub>, CO can be converted to CO<sub>2</sub> with 100% H<sub>2</sub> selectivity with this Ce<sub>0.65</sub>Fe<sub>0.33</sub>Pd<sub>0.02</sub>O<sub>1.815</sub> catalyst.

## 4. Conclusions

In summary, we have described a new low temperature sonochemical route to synthesize higher percentage  $Fe^{3+}$  substituted ceria *i.e.*  $Ce_{1-x}Fe_xO_{2-\delta}$  ( $0 \le x \le 0.45$ ) and both  $Pd^{2+}$  and  $Fe^{3+}$  ion substituted ceria *i.e.*  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  using diethylenetriamine as a complexing agent.  $Ce_{0.67}Fe_{0.33}O_{2-\delta}$  shows high OSC of ~0.31 [O]/mol and even without noble metal, it is a good catalyst for CO oxidation and WGS reaction. Due to interaction of redox potentials of  $Pd^{2+/0}$ ,  $Fe^{3+/2+}$  with  $Ce^{4+/3+}$ ,  $Ce_{0.65}Fe_{0.33}Pd_{0.02}O_{2-\delta}$  showed high OSC at low temperature (~120 °C) and also showed high activity for low-temperature CO oxidation and WGS reaction. Interaction of  $Pd^{2+/0}$  redox couple with  $Fe^{3+/2+}$  and  $Ce^{4+/3+}$  redox couples is also reflected in high current density in electrochemical  $O_2$  evolution.

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## References

- 1 H. Inaba and H. Tagawa, Solid State Ionics, 1996, 83, 1-6.
- 2 A. Trovarelli, Catal. Rev. Sci. Eng., 1996, 38, 439-20.
- 3 M. S. Hegde, G. Madras and K. C. Patil, *Acc. Chem. Res.*, 2009, **42**, 704–12.
- 4 Q. Fu, H. Saltsbarg and M. Flytzani-Stephanopoulos, *Science*, 2003, **301**, 935–38.
- 5 E. P. Murray, T. Tsai and S. A. Barnett, Nature, 1999, 400, 19-51.
- 6 A. Corma, P. Atienzar, H. Gracia and J. Y. Chane-Ching, *Nat. Mater.*, 2004, **3**, 394–97.
- 7 X. J. Yu, P. B. Xie and Q. D. Su, *Phys. Chem. Chem. Phys.*, 2001, **3**, 5266–5269.
- 8 A. H. Morshed, M. E. Moussa, S. M. Bedir, R. Leonard, S. X. Iiu and N. Elmasry, *Appl. Phys. Lett.*, 1997, **70**, 1647–1649.
- 9 N. W. Cant, P. C. Hicks and B. S. Lenon, J. Catal., 1978, 54, 372-383.
- 10 J. T. Kummer, J. Phys. Chem., 1986, 90, 4747-4752.
- 11 R. Pérez-Hernán, dez, F. Aguilar, A. Gómez-Cortés and G. Díaz, *Catal. Today*, 2005, **107–108**, 175–180.
- 12 Y. Guo, G. Lu, Z. Zhang, S. Zhang, Y. Qi and Y. Liu, *Catal. Today*, 2007, **126**, 296–302.
- 13 H. C. Yao and Y. F Yao, J. Catal., 1984, 86, 254-265.
- 14 P. Fornasiero, R. Di Monte, G. Ranga Rao, J. Kaspar, S. Meriani, A. Trovarelli and M. Graziani, J. Catal., 1995, 151, 168–177.
- 15 R. Di Monte and J. Kaspar, J. Mater. Chem., 2005, 15, 633-648.
- 16 T. Baidya, A. Gayen, M. S. Hegde, N. Ravishankar and L. Dupont, J. Phys. Chem. B, 2006, 110, 5262–5272.
- 17 T. Baidya, A. Marimuthu, M. S. Hegde, N. Ravishankar and G. Madras, J. Phys. Chem. C, 2007, 111, 830–839.
- 18 T. B. Nguyen, J. P. Deloume and V. Perrichon, *Appl. Catal.*, A, 2003, 249, 273–284.
- 19 T. Baidya, A. Gupta, P. A. Deshpandey, G. Madras and M. S. Hegde, J. Phys. Chem. C, 2009, 113, 4059–4068.
- 20 P. Singh, M. S. Hegde and J. Gopalakrishnan, *Chem. Mater.*, 2008, 20, 7268–7273.
- 21 P. Singh and M. S. Hegde, Chem. Mater., 2009, 21, 3337-3345.
- 22 Y. Nagai, T. Yamamoto, S. Yoshida, T. Nonaka, T. Okamoto, A. Suda and M. Sugiura, *Catal. Today*, 2002, **74**, 225–234.
- 23 F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd ed. Wiley Eastern: New Delhi, India, 1972; p. 841, 1072.
- 24 T. Baidya, G. Dutta, M. S. Hegde and U. V. Waghmare, *Dalton Trans.*, 2009, 455–464.
- 25 S. Roy, A. Marimuthu, M. S. Hegde and G. Madras, *Appl. Catal.*, *B*, 2007, **71**, 23–31.
- 26 P. Bera, K. C. Patil, V. Jayaram, G. N. Subbanna and M. S. Hegde, J. Catal., 2000, 196, 293–301.
- 27 F. A. Cotton and G. Wilkinson, Advanced Inorganic Chemistry, 3rd ed. Wiley Eastern: New Delhi, India, 1972; p. 860.
- 28 A. Gupta, A. Kumar, U. V. Waghmare and M. S. Hegde, *Chem. Mater.*, 2009, **21**, 4880–4891.
- 29 C. Liang, Z. Ma, H. Lin, L. Ding, J. Qiu, W. Frandsen and D. Su, J. Mater. Chem., 2009, **19**, 1417–1424.
- 30 P. Singh and M. S. Hegde, J. Solid State Chem., 2008, 181, 3248–3256.
- 31 G. Li, R. L. Smith and H. Inomata, J. Am. Chem. Soc., 2001, 123, 11091-11092.
- 32 (a) H. L., H. Tu, B. Zhao, Y. Wu and K. Hu, Solid State Ionics, 2007, 177, 3467–3472; (b) B. Matovic, Z. Dohcevic-Mitrovic, M. Radovic, Z. Brankovic, G. Brankovic, S. Boskovic and Z. V. Popovic, J. Power Sources, 2009, 193, 146–149; (c) T. Dhannia, S. Jayalekshmi, M. C. SanthoshKumar, T. Prasada Rao and A. Chandra Bose, J. Phys. Chem. Solids, 2010, 71(7), 1020–1025; (d) O. D. Jayakumar, A. Vinu, K. V.

Guduru, T. Sakuntala and A. K. Tyagi, *J. Nanosci. Nanotechnol.*, 2010, **10**(4), 2299–2303.

- 33 L. Yin, Y. Wang, G. Pang, Y. Koltypin and A. Gedanken, J. Colloid Interface Sci., 2002, 246, 78–84.
- 34 T. Roisnel and J. Rodríguez-Carvajal, "WinPLOTR: a windows tool for powder diffraction pattern analysis,", *Mater. Sci. Forum*, 2001, **118**, 378.
- 35 R. D. Shannon, Acta Crystallogr., Sect. A: Cryst. Phys., Diffr., Theor. Gen. Crystallogr., 1976, 32, 751–767.
- 36 B. D. Cullity, *Elements of X-ray Diffraction*, 2nd ed., Addison-Wesley, Reading, MA, 1978 p. 281.
- 37 G. Caglioti, A. Paoletti and F. P. Ricci, *Nuclear Instruments*, 1958, 3, 223.

- 38 C. Liu, L. Luo and X. Lu, Kinet. Catal., 2008, 49(5), 676-681.
- 39 C. N. R. Rao, D. D. Sarma, S. Vasudevan and M. S. Hegde, Proc. R. Soc, Lond., 1979, A 367, 239–252.
- 40 A. Kotani and H. Ogasawara, J. Electron Spectrosc. Relat. Phenom., 1992, 60, 257-299.
- 41 M. Brun, A. Berthet and J. C. Bertolini, J. Electron Spectrosc. Relat. Phenom., 1999, 104, 55–60.
- 42 C. J. Powell and P. E. Larson, Appl. Surf. Sci., 1978, 1, 186-201.
- 43 J. H. Scofield, J. Electron Spectrosc. Relat. Phenom., 1976, 8, 129– 137.
- 44 D. R. Penn, J. Electron Spectrosc. Relat. Phenom., 1976, 9, 29-40.
- 45 K Suresh, K. C. Patil and J. Mater, Sci. Lett., 1993, 12, 572-574.