Noble metal ionic catalysts: correlation of increase in CO oxidation activity with increasing effective charge on Pd ion in Pd ion substituted $Ce_{1-x}M_xO_{2-\delta}$ (M = Ti, Zr and Hf)

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Pd ion substituted $Ce_{1-x}M_xO_{2-\delta}$ (M = Ti, Zr, Hf) have been prepared by a single step solution combustion method. Two atom% Pd ion substitution in the title compounds is confirmed by X-ray diffraction (XRD) and Pd ion charge state and redox properties have been determined by X-ray photoelectron spectroscopy (XPS) and H₂/TPR studies. While Pd ion in CeO₂ (Ce_{0.98}Pd_{0.02}O_{2- δ}) showed higher catalytic activity for CO oxidation than Pd metal impregnated over CeO₂, further increase in the catalytic activity is observed with Pd ion in Ce_{1-x}Ti(Hf)_xO₂ and a decrease in the activity with Pd ion in Ce_{1-x}Zr_xO₂. Effective charge on Pd ion could be varied by its substitution in these solid solutions Ce_{1-x}M_xO₂ (M = Ti, Zr & Hf) and also in TiO₂ compared to Pd ion in PdO. Effective positive charge on Pd ion is determined from the core level binding energy shift of Pd(3d_{5/2}) peak with respect to Pd metal. Rate of CO oxidation increased and activation energy decreased with increase in effective charge on the Pd ion in the Pd ion substituted fluorites.

1. Introduction

Cerium dioxide is a reducible oxide, crystallizing into fluorite structures. The lattice oxygen is sufficiently labile to be extracted by CO to CO_2 and the oxide ion vacancy thus created can be replenished by feed oxygen:^{1,2}

$$\begin{split} \mathrm{CeO}_2 + \delta\mathrm{CO} &\to \mathrm{CeO}_{2-\delta} + \delta/2\mathrm{CO}_2 \\ \mathrm{CeO}_{2-\delta} + \delta/2 \ \mathrm{O}_2 &\to \mathrm{CeO}_2. \end{split}$$

The smaller the size of CeO₂ crystallites, the higher the extent of δ (oxygen) which can be utilized for CO oxidation. The fluorite structure of CeO₂ is retained under these redox conditions. The extent of oxygen reversibly exchanged is defined as the oxygen storage capacity (OSC), a property that is important for exhaust catalysis.² Enhanced OSC (δ) can be achieved by the substitution of Zr in CeO₂.³⁻⁵ An increase in OSC of Ce_{1-x}Zr_xO₂ arises due to a higher lability of oxygen in the distorted oxygen sublattice of cubic Ce_{1-x}Zr_xO₂. As Zr⁴⁺ is a smaller ion, coordination of Zr⁴⁺ is found to be 4 + 4 instead of the ideal 8 coordination. The Ce–O bond length is 2.34 Å in CeO₂ and, upon Zr substitution, 4 long Zr–O (Ce–O) and 4 short Zr–O (Ce–O) bonds are formed compared to the single Ce–O distance. The oxygen associated with long Ce–O (Zr–O) bonds is weak, susceptible to extraction by CO, thus giving a higher OSC.^{6,7}

 Ti^{4+}/Hf^{4+} ions can also be substituted for Ce ions, forming $Ce_{1-x}Ti_xO_2$ (x = 0.1–0.4) and $Ce_{1-x}Hf_xO_2$ (x = 0.5) retaining fluorite structure.⁸⁻¹¹ Enhancement of OSC is obtained with these metal ion substitutions in CeO₂.

 $Ce_{1-x}M_xO_{2-\delta}$ (M = Cu, Pd, Pt, Rh) showed higher catalytic activity, and also higher reducibility, due to the electronic interaction between M²⁺ ions in CeO₂.¹²⁻¹⁵ Substitution of Pd ion in $Ce_{1-x}Ti_xO_2$ showed that the lattice oxygen is much more labile than Pd ion in CeO₂. Indeed, substitution of Pt or Pd ion in $Ce_{1-x}Ti_xO_2$ showed much higher CO oxidation and NO reduction activity than Pd ion in CeO2.9,16 However, a lower activity for CO oxidation is observed over $Pd/Ce_{1-x}Zr_xO_2$ than Pd/CeO_2 .¹⁷ $Ce_{1-x}Hf_xO_2$ solid solution has been reported recently and it was shown that $Ce_{1-x}Hf_xO_2$ is more reactive toward CO oxidation than $Ce_{1-x}Zr_xO_2$.¹⁰ Since both Zr^{4+} and Hf^{4+} ions have similar ionic radii (Zr⁴⁺ 8CN 0.84 Å; Hf⁴⁺ 8CN 0.83 Å),¹⁸ completely different CO oxidation activity of Zr and Hf substituted Pd/CeO₂ could not be explained. Pd ion substituted $Ce_{1-x}M_xO_2$ (M = Zr and Hf) is not reported in the literature. Substitution of Ti, Zr and Hf give similar structural modification of the oxide sublattice in CeO₂ and if the Pd ion is substituted in these mixed oxides, effective charge on the Pd ion can be varied in different oxides (supports) because electronegativity varies in the decreasing order Ti > Hf > Zr (Alred-Rochow electronegativity scale).¹⁹

In the present study we have shown a correlation between CO oxidation activity and effective positive charge on Pd ion in $Ce_{1-x}M_xO_2$ (Ti, Zr and Hf). A detailed structural analysis has been carried out by XRD, XPS and H₂-TPR study. We find that CO oxidation activity increases with increase in the effective charge on the Pd ion.

2. Method

2.1 Experiments

 $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ was prepared by a single step solution combustion method using ammonium ceric nitrate, $((NH_4)_2Ce(NO_3)_6)$, palladium chloride, $(PdCl_2)$ and oxalyl dihydrazide $(C_2H_6N_4O_2)$

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in a 0.98:0.02:2.35 molar ratio. In a typical preparation, 10 g of $(NH_4)_2Ce(NO_3)_6$, 0.066 g of PdCl₂ and 5.74 g of $C_2H_6N_4O_2$ were taken in a 300 ml crystallizing dish, made into clear aqueous solution and heated in a muffle furnace at 400 °C. The solution boils and after complete dehydration it ignites into a flame rising the temperature to ~1000 °C, dwelling for 30–40 s and quenches to 400 °C in a few seconds. Ti_{0.99}Pd_{0.01}O₂₋₆ was prepared from titanyl nitrate (TiO(NO₃)₂), PdCl₂ and glycene (C₂H₅NO₂) precursors with 0.99:0.01:1.11 molar ratio. TiO(NO₃)₂ was prepared by dissolving titanyl hydroxide (TiO(OH)₂) in minimum amount of HNO₃. TiO(OH)₂ was prepared by hydrolyzing TiCl₄ in H₂O at 4 °C. Chloride ion was removed by repeated washing of TiO(OH)₂ in deionized water.

 $Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}$ was synthesized in a single step combustion taking $(NH_4)_2Ce(NO_3)_6$, $PdCl_2$, $TiO(NO_3)_2$ (in solution) and $C_2H_3NO_2$ in the mole ratio 0.73:0.02:0.0.25:2.42. For preparation of the compound, 10 g $(NH_4)_2Ce(NO_3)_6$, 1.17 g $TiO(NO_3)_2$ (in solution), 0.089 g $PdCl_2$ and 4.16 g $C_2H_5NO_2$ were taken.

 $Ce_{1-x-y}Zr_xPd_yO_{2-\delta}$ (x = 0.15, 0.25 and 0.4; y = 0.02) was prepared from (NH₄)₂Ce(NO₃)₆·6H₂O, Zr(NO₃)₄, PdCl₂ and C₂H₆N₄O₂ as a fuel.

 $Ce_{0.73}Hf_{0.25}Pd_{0.02}O_2$ was prepared with $(NH_4)_2Ce(NO_3)_6\cdot 6H_2O$, $Hf(NO_3)_4$, $PdCl_2$ and $C_2H_5NO_2$ in a 0.73:0.25:0.02:2.5 molar ratio; 10.0 g, 2.0 g, 0.089 g and 4.4 g of the respective precursors were used for the preparation. $Ce_{0.58}Hf_{0.40}Pd_{0.02}O_{2-\delta}$ was also prepared following a similar procedure. Hafnium nitrate was made using $HfCl_4$ precursor. Initially the required amount of $HfCl_4$ was hydrolyzed in water giving a white precipitate of hafnium hydroxide which was dissolved in minimum volume of concentrated HNO_3 .

Similarly, $Ce_{0.7}M_{0.25}Pd_{0.05}O_{2-\delta}$ (M = Ti, Zr & Hf) have been prepared by taking a stoichiometric amount of respective metal salts and the fuel.

X-Ray diffraction (XRD) data of all the Pd-substituted samples were recorded on a Philips X'Pert diffractometer at a scan rate of 0.12 deg min⁻¹ with a 0.02° step size in the 2θ range between 20 and 100 degrees. The refinement was done using FullProf-fp2k program varying 17 parameters simultaneously.

X-Ray photoelectron spectra (XPS) of PdO, $Ti_{0.99}Pd_{0.01}O_{2-\delta}$, $Ce_{0.98}Pd_{0.2}O_{2-\delta}$, $Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}$, $Ce_{1-x-y}Zr_xPd_yO_{2-\delta}$ (x = 0.15, 0.25 and 0.4; y = 0.02) and $Ce_{1-x-y}Hf_xPd_yO_{2-\delta}$ (x = 0.25 and 0.4; y = 0.02) oxides were recorded in a Thermo Fisher Scientific Multilab 2000 (England) with Al K α radiation (1486.6 eV). Binding energies reported here are with reference to graphite at 284.5 eV or Ag(3d_{5/2}) at 368.2 eV and they are accurate within ± 0.1 eV. Oxide samples were ground with 30% by wt of graphite powder and made into thin pellets at room temperature and XPS data were recorded. There was no charging of the oxide samples. The compounds were reduced in 5% H₂/Ar for 1 h at 500 °C in a quartz tube. XPS of freshly reduced pellets were also recorded.

Hydrogen uptake experiments as a function of temperature were carried out by passing 5% H_2 in Ar at 30 ml min⁻¹ flow rate over 50 mg of oxide and the volume of H_2 uptake is detected by a TCD detector, which is calibrated against the uptake of H_2 with known amounts of CuO.

The catalytic test was done in a temperature programmed reaction (TPR) system equipped with a quadrupole mass spectrometer SX200 (VG Scientific Ltd., England) for product analysis in a packed bed tubular quartz reactor (dimension 25 cm \times 0.4 cm) at atmospheric pressure. Typically, 50 mg of the catalyst (40/ 80 mesh size) diluted with SiO₂ (30/60 mesh size) was loaded in the reactor to get a column length of 1.1 cm and endings were plugged with ceramic wool. For all the reactions, the total flow was kept fixed at 100 sccm to achieve a gas hourly space velocity (GHSV) of 43 000 h⁻¹. CO and O₂ were taken in 2 : 2 vol% for all the catalytic reactions. Before the catalytic test, the as-prepared catalyst was heated in O₂ flow at 300 °C for 1 h followed by degassing in He flow to the experimental temperature. The reactions were carried out as a function of temperature with a linear heating rate of 5° min⁻¹.

Nonlinear least square technique in Polymath 5.1 software is used to test the model. In this technique the optimized values are obtained by minimizing the sum of squared differences of the experimental rate and calculated rate:

$$\sigma^{2} = \sum_{i=1}^{N} \frac{\left(r_{\exp} - r_{\text{model}}\right)^{2}}{N - K}$$

where N = Number of runs; K = Number of parameter to be optimized.

2.2 Theory: DFT calculations

We have simulated the interaction of isolated Pd (metal Pd⁰ and Pd ion with varying charge on Pd ions) with CO molecule using a large cell of a = 15.875 Å. A large cell is taken so as to simulate isolated systems of (Pd^{δ_+} + CO). CO molecule is placed with C at a distance of 1.86 Å from Pd. Our total energy calculations are based on the ABINIT^{20,21} implementation of density functional theory (DFT)²² and exchange-correlation energy within the local density approximation (LDA).²³ It involves solving the Kohn-Sham equations²⁴ by a fixed potentialbased iterative conjugate-gradient minimization²⁵ of one-electron energies in the ground-state and achieves the self consistency of Kohn-Sham potential.²⁶ The potential of the nucleus and the core electrons was approximated with pseudopotentials: Fritz-Haber-Institute pseudopotentials were used for O, Pd and Goedecker-Teter-Hutter pseudopotential for C. We used an energy cutoff of 25 Ha, $2 \times 2 \times 2$ Monkhorst–Pack mesh²⁷ for Brillouin zone integration. Ionic relaxations were performed using molecular dynamics with viscous damping. We have performed Hirshfeld atomic charge analysis to understand the net charge on atoms and charge transfers between atoms.²⁸ To simulate our systems with varying charge on Pd, we have placed (Pd^{δ +} + CO) in the cell and varied the total number of electrons in the cell depending on the charge on Pd. The cell is deficient of δ electrons for creating a system with Pd⁸⁺ ion. To treat systems with Pd^{0.5+}, Pd^{1.0+}, Pd^{1.5+} and Pd²⁺, we have removed $\delta = 0.5, 1.0, 1.5, 2.0$ electrons from the cell. We have used the 'charge' option of the ABINIT code, to treat systems with missing δ electrons per cell. This establishes the charge balance between the number of electrons filling the bands and the nominal charge associated with the atomic cores: the number of electrons in the cell is δ + the number of valence electrons. To treat a neutral system, we set charge = 0 and for a system missing one electron per unit cell, we set charge = +1 and for the systems, Pd^{0.5+}, Pd^{1.0+}, Pd^{1.5+} and Pd²⁺ (with CO) we use charge = +0.5, +1.0, +1.5 and +2.0 (Hirshfeld charge analysis in fact shows that the total net charge on the above systems (Pd^{δ^+} + CO) are 0.500194, 1.000152, 1.500132, 2.000124, as expected).

3. Results

3.1 XRD studies

5500

4400

All the compounds crystallize in fluorite structure and the XRD profiles are refined by Rietveld refinement method. Fig. 1 shows the Rietveld refined XRD patterns of Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2- δ}, Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2- δ} and Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{2- δ}. Similarly, refinements were carried out for all the Pd substituted as well as unsubstituted oxides and the refined structural parameters are given in Table 1. R factor is low and χ^2 is nearly 1 for all the compounds. Zr⁴⁺ (8CN 0.84 Å) and Hf⁴⁺ (8CN 0.83 Å) ions have larger ionic radius than Pd²⁺ (8CN 0.64 Å) and Ti⁴⁺ (8CN 0.74 Å). Thus further decrease of the cell parameter is expected if Pd ion is substituted in the Ce⁴⁺ site in the oxide lattice. The cell parameter decreases with Pd ion substitution in

 Table 1
 Rietveld refined parameters of unsubstituted and Pd substituted compounds

Compounds	$R_{ m Bragg}$	$R_{ m F}$	χ^2	a/Å
CeO ₂	1.17	0.90	1.02	5.4131(4)
$Ce_{0.98}Pd_{0.02}O_{2-\delta}$	3.06	2.15	1.42	5.4122(6)
$Ce_{0.75}Ti_{0.25}O_2$	2.93	2.07	1.23	5.3912(9)
$Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}$	2.90	1.95	1.22	5.3992(7)
$Ce_{0.75}Zr_{0.25}O_2$	2.03	1.15	1.32	5.3515(8)
$Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2-\delta}$	1.48	1.25	1.43	5.3417(6)
$Ce_{0.6}Zr_{0.4}O_2$	2.72	1.65	1.50	5.3079(8)
$Ce_{0.58}Zr_{0.40}Pd_{0.02}O_{2-\delta}$	1.79	1.14	2.30	5.2959(8)
$Ce_{0.75}Hf_{0.25}O_2$	1.69	1.30	0.80	5.3631(3)
$Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{2-\delta}$	0.94	0.86	1.27	5.3484(9)
$Ce_{0.6}Hf_{0.4}O_2$	2.08	1.46	0.78	5.3181(4)
$Ce_{0.58}Hf_{0.40}Pd_{0.02}O_{2-\delta}$	2.69	1.92	1.22	5.3108(5)

 $Ce_{1-x}Zr_xO_2$ and $Ce_{1-x}Hf_xO_2$. Refinement was carried out taking zero occupancy of Pd in the Pd ion substituted oxides and R factor increased if it is not occupying Ce/Ti site in the lattice confirming incorporation of Pd ion. The increase in cell parameter in the case of 2%Pd in Ce_{0.75}Ti_{0.25}O₂ compared to Ce_{0.75}Ti_{0.25}O₂ may be due to lower (4 to 6) local coordination of Ti. Variation of cell parameter with respect to the pure oxide confirms the substitution of Pd ion in these mixed oxides. Pd metal or PdO could not be detected in any of the XRD patterns. To see if small amount of Pd²⁺ ion taken in the preparation is thrown out as Pd metal or PdO, the XRD patterns were 20 times magnified in the Y-scale. Fig. 2(a) shows the magnified XRD patterns of $Ce_{0.98}Pd_{0.02}O_{2-\delta}$, $Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}$, $Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{2-\delta}$, $Ce_{0.58}Hf_{0.40}Pd_{0.02}O_{2-\delta}$ and $Ce_{1-x-y}Zr_xPd_yO_{2-\delta}$ (x = 0.15 and 0.25; y = 0.02). There is no peak at 40.2° due to Pd(111) in any of the compounds. Diffraction lines due to PdO were not observed in the Ti, Zr and Hf substituted compounds. Formation of $Ce_{_{0.98}}Pd_{_{0.02}}O_{_{2-\delta}},^{29}$ $Ti_{_{0.99}}Pd_{_{0.01}}O_{_{2-\delta}}{}^{30}$ and $Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}^{16}$ solid solutions have been discussed in our earlier studies and substitution of Pd ion is confirmed by TEM and other experimental techniques.

To confirm that Pd is ionically substituted and not present as fine PdO particles, we reduced $Ce_{0.73}M_{0.25}Pd_{0.02}O_{2-\delta}$ (M = Ti, Zr & Hf) in H₂ at 500 °C for 1 h and in Fig. 2(b) XRD pattern of the reduced samples with 10 times magnification in the *Y* scale are shown. The Pd(111) peak intensity at $2\theta = 40.2$ is almost to the noise level. However, $Ce_{0.75}Zr_{0.25}O_2 + 2atom\%$ PdO mixture on reduced at 500 °C for 1 h indeed show prominent Pd(111) peak (see Fig. 2(b)). Thus, the Pd ion is substituted in these oxides and they are represented by $Ce_{0.73}M_{0.25}Pd_{0.02}O_{2-\delta}$ (M = Ti, Zr & Hf).

Crystallite sizes were calculated following Scherrer formula and half widths were taken from U, V, W values from Rietveld refinement with FWHM, $\beta = [U\tan^2\theta + V\tan\theta + W]^{\frac{1}{2}}$. Crystallite sizes are in the range of 6–11 nm. Ce_{0.98}Pd_{0.02}O_{2- δ} crystallites are bigger, ~30 nm. BET surface areas are in the range of 20–30 m² g⁻¹ as can be seen from Table 2.

3.2 Hydrogen uptake studies

The reactivity of lattice oxygen of oxide catalysts is generally characterized by H_2/TPR measurements. Fig. 3(a) shows H_2 -TPR of CeO₂, Ce_{0.75}Ti_{0.25}O₂, Ce_{0.75}Zr_{0.25}O₂ and Ce_{0.75}Hf_{0.25}O₂. In the case of CeO₂, the peak at ~350 °C occurs due to the reduction of Ce⁴⁺ ions on the surface and the bulk reduction peak is observed above 600 °C.¹ On substitution of Ti, Zr or Hf ion in CeO₂ forming



Table 2Crystallite size from Scherrer formula and BET surface area ofPd substituted catalysts

Catalysts	Crystallite size from Rietveld/nm	BET surface area/m ² g ⁻¹	
$Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}$	8.7	24	
$Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{2-\delta}$	6.3	29	
$Ce_{058}Hf_{0.4}Pd_{0.02}O_{2-\delta}$	10.2		
$Ce_{0.98}Pd_{0.02}O_{2-\delta}$	30	18	
$Ce_{0.83}Zr_{0.15}Pd_{0.02}O_{2-\delta}$	8.2	25.3	
$Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2-\delta}$	6.3	26	
$Ce_{0.58}Zr_{0.4}Pd_{0.02}O_{2-\delta}$	11.1	24	



 $Ce_{1-x}M_xO_2$ (Ti, Zr & Hf) solid solutions, significantly higher extent of reduction is observed in comparison with pure CeO₂ (Fig. 3a). Total oxygen removed from the lattice by hydrogen up to 700 °C as given in Table 3 reflect the role of Ti, Zr and Hf substitution in CeO₂.

On Pd ion substitution in the above oxides, the temperature of reduction decreases significantly. TPR of PdO is also given for comparison (Fig. 3b–c). H₂ uptake with PdO occur at ~70 °C (see in Fig. 3b) and it shows a negative peak due to release of H₂ from PdH_x.³¹ 2atom% PdO mixed with Ce_{0.75}Zr_{0.25}O₂ also show PdO like H₂/TPR profile. However, the reduction behavior of Pd ion substituted oxides is different depending on the particular oxide and it does not show any negative



Fig. 3 (a) H₂-TPR profile of CeO₂, Ce_{0.75}Ti_{0.25}O₂, Ce_{0.75}Zr_{0.25}O₂ and Ce_{0.75}Hf_{0.25}O₂. (b) H₂ TPR profile of PdO and 2atom% PdO + Ce_{0.75}Zr_{0.25}O₂ (physical mixture). (c) H₂-TPR of Ce_{0.98}Pd_{0.02}O_{2-\delta}, Ti_{0.99}Pd_{0.01}O_{2-\delta}, Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}, Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{2-\delta}.

peak confirming the absence of PdO. Fig. 3(c) shows the H₂-TPR profile of $Ti_{0.99}Pd_{0.01}O_{2-\delta}$, $Ce_{0.98}Pd_{0.02}O_{2-\delta}$, $Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}$, $Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2-\delta}$ and $Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{2-\delta}$ oxides. Total H/Pd ratio was estimated by integrating the area under the curve up to 150 °C and the values are given in Table 3. Total OSC of the Pd ion substituted compounds up to 700 °C are also given in the same Table. Ti_{0.99}Pd_{0.01}O_{2- δ} gets reduced at as low as 0 °C compared to the cerium containing compounds. However, reduction occurs above 50 °C over the Pd ion substituted $Ce_{1-x}M_xO_2$ oxides. The reduction of Pd ion substituted oxides is reflected in the H/Pd ratio. H/Pd ratio for PdO is 2 corresponding to PdO + $H_2 \rightarrow$ $Pd + H_2O$. For $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ and $Ti_{0.99}Pd_{0.01}O_{2-\delta}$, H/Pd ratio is 4. Since H/Pd ratio is 4, it is expected that Pd²⁺ ion gets reduced to Pd⁰ at that temperature and a small extent of CeO₂/TiO₂ surface reduction also occur at low temperature. However, Pd ion substituted $Ce_{1-x}M_xO_2$ induces larger hydrogen consumption compared to $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ and $Ti_{0.99}Pd_{0.01}O_{2-\delta}$. This is attributed

Catalysts	Composition of reduced phase (up to 700 °C)	OSC/cc g ⁻¹	H/Pd ratio for low temperature (< 150 °C) peaks	%Ce ⁴⁺ /Ce ⁴⁺ +Ti ⁴⁺ reduction (< 150 °C)
CeO ₂	CeO _{1.07}	3.9	0	0
$Ce_{0.75}Ti_{0.25}O_2$	$Ce_{0.75}Ti_{0.25}O_{1.79}$	31.6	0	0
$Ce_{0.75}Zr_{0.25}O_2$	$Ce_{0.75}Zr_{0.25}O_{1.67}$	46.3	0	0
$Ce_{0.6}Zr_{0.4}O_2$	$Ce_{0.6}Zr_{0.4}O_{1.63}$	54.4	0	0
$Ce_{0.75}Hf_{0.25}O_2$	$Ce_{0.75}Hf_{0.25}O_{1.87}$	16	0	0
$Ti_{0.99}Pd_{0.01}O_{2-\delta}$	$Ti_{0.99}Pd_{0.01}O_{1.94}$	11.2	4.0	_
$Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}$	$Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{1.79}$	28.8	17	15.3
$Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{2-\delta}$	$Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{1.78}$	25.1	12	13.7
$Ce_{0.58}Hf_{0.40}Pd_{0.02}O_{2-\delta}$	$Ce_{0.58}Hf_{0.40}Pd_{0.02}O_{1.83}$	18	13	19
$Ce_{0.98}Pd_{0.02}O_{2-\delta}$	$Ce_{0.98}Pd_{0.02}O_{1.94}$	5.2	4.0	2
$Ce_{0.83}Zr_{0.15}Pd_{0.02}O_{2-\delta}$	$Ce_{0.83}Zr_{0.15}Pd_{0.02}O_{1.87}$	14.3	6.5	5.3
$Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2-\delta}$	$Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{1.74}$	33.8	13	15.1
$Ce_{0.58}Zr_{0.4}Pd_{0.02}O_{2-\delta}$	$Ce_{0.58}Zr_{0.4}Pd_{0.02}O_{1.73}$	36.1	14	20.7
PdO	Pd	_	2.0	—

Table 3 Total OSC and H/Pd ratio for low temperature peak (up to 150 °C)

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to the easy reduction of Ti ion along with Ce ion in CeO₂ matrix in presence of Pd. H/Pd ratio is as high as 17 from the low temperature peak in Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2- δ} indicating greater extent of oxide reduction. H/Pd ratio for 15, 25 and 40% Zr ion substituted compounds are 6.5, 13 and 14, respectively. Similarly, H/Pd ratio for 25 and 40% Hf substituted compounds are 12 and 13, respectively. Percentage of Ce⁴⁺ ion reduction below 150 °C in the Pd substituted compounds is given in Table 3. While Ce⁴⁺ ion is not easily reduced in the pure oxide, it gets easily reduced in presence of Pd ion at a lower temperature indicating activation of lattice oxygen. About 15% of Ce⁴⁺ ion gets reduced in the mixed oxide in presence of Pd ion. Large H/Pd ratio observed at much lower temperature than the corresponding unsubstituted oxide clearly demonstrated higher oxygen lability.

The low temperature hydrogen uptake peak in the noble metal dispersed CeO₂ catalysts at ~80–200 °C is due to reduction of oxidized noble metal as reported in the literature.³²⁻³⁶ Higher amount of hydrogen consumption at a lower temperature was ascribed to the hydrogen spill over phenomena of adsorbed hydrogen on to the oxide surface. In the Pd ion substituted catalysts every ion is active for adsorption. Since every Pd ion is able to act as active site for adsorption, the amount of H₂ spilled over to the oxide support is high. In our earlier study we had shown that Ce_{0.73} Ti_{0.25}Pd_{0.02}O_{2- δ} reduced at 100 °C, Pd as well as Ce and Ti

ions in a partially reduced state.¹⁶ Recently, we have experimentally as well as theoretically showed that Pt^{2+} ion substituted in CeO₂ can stabilize 6 hydrogen atoms per Pt atom.³⁷ Similarly, Pd ion can induce more H₂ adsorption at lower temperature resulting in higher H/Pd ratio. Therefore, variation in the hydrogen uptake is likely due to variation in the nature of Pd ion in the oxides.

3.3 Catalytic activity

3.3.1 CO oxidation. Fig. 4(a) shows the CO oxidation profile over PdO, $Ti_{0.99}Pd_{0.01}O_{2-\delta}$, $Ce_{0.98}Pd_{0.98}O_{2-\delta}$, $Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}$, $Ce_{1-x-0.02}Zr_xPd_{0.02}O_{2-\delta}$ (x = 0.15 and 0.25) and $Ce_{1-x-0.02}Hf_xPd_{0.02}O_{2-\delta}$ (x = 0.25). CO oxidation reactions were carried out with CO: O_2 ratio of 2: 2 vol%. Amount of Pd ion 2atom% Pd ion is substituted for Ce in $Ce_{1-x}M_xO_2$ and 1atom% Pd in TiO₂ is nearly the same. Accordingly, in 50 mg of each of the catalysts, amount of Pd is 0.65 ± 0.05 mg. Table 4 shows the temperature at which 10% CO get converted to CO₂ (T_{10}). T_{10} has been considered to compare the reactivity of the compounds for CO oxidation because the rate of CO oxidation is linear with the weight of the catalyst at 10% CO conversions. Fig. 4(b) shows the Arrhenius plots for all the compounds and the activation energy values are presented in Table 4. CO oxidation occurs at the lowest temperature over $Ti_{0.99}Pd_{0.01}O_{2-\delta}$ starting at 45 °C having T_{10} of

Table 4 $Pd(3d_{5/2})$ core level binding energy, T_{10} for CO oxidation along with the activation energies over the Pd substituted catalysts

Catalysts	XPS binding energy/eV(Pd(3d _{5/2}))	CO oxidation $T_{10}/^{\circ}C$	$E_{\rm a}/{\rm kcal}~{\rm mol}^{-1}$	
$Ce_{0.78}Sn_{0.20}Pd_{0.02}O_{2-\delta}^{a}$	338.0	50	10.5	
$Ti_{0.99}Pd_{0.01}O_{2-\delta}$	337.9	80	13.1	
$Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}$	337.8	75	13.0	
$Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{2-\delta}$	_	100	13.9	
$Ce_{0.58}Hf_{0.40}Pd_{0.02}O_{2-\delta}$	337.9	90	13.5	
$Ce_{0.98}Pd_{0.02}O_{2-\delta}$	337.7	120	16.0	
$Ce_{0.83}Zr_{0.15}Pd_{0.02}O_{2-\delta}$	337.6	140		
$Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2-\delta}$	337.4	194	24.0	
$Ce_{0.58}Zr_{0.4}Pd_{0.02}O_{2-\delta}$	337.1	220	34.0	
PdO	336.6	247		
Pd metal	335.1	_		
PdCl ₂	338.0	_		
$Pd(NO_3)_2$	338.2	_	_	

" Complete study to be published separately.

80 °C. Clearly, $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ is less reactive than $Ti_{0.99}Pd_{0.01}O_{2-\delta}$ for CO oxidation. T_{10} over $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ is 120 °C and the value decreases to 75 °C on 25% Ti substitution in CeO₂. Substitution of Zr decreases the activity compared to $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ for CO oxidation. T_{10} increases from 140, 194 and 220 °C over 15, 25 and 40% Zr substituted catalysts show enhancement of catalytic activity unlike Zr substituted catalyst. It even shows better catalytic reactivity than $Ce_{0.98}Pd_{0.02}O_{2-\delta}$. Further, CO oxidation activity increases with increase of Hf ion substituted in CeO₂ and the T_{10} values are 100 and 90 °C over 25 and 40% Hf substituted compounds, respectively.

To confirm if CO adsorption is hindered on Pd ion site by O_2 molecule and responsible for the shift to higher temperature for Zr substituted catalyst, CO oxidation at different partial pressures over Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2- δ} was carried out. Even at different partial pressures, CO oxidation profile remains to be almost similar. CO oxidation starts at ~120 °C at all the pressures and the variation in T₁₀ is not significant when partial pressures were varied from 1 to 5 vol% O₂ along with 2 vol% of CO. Therefore, CO adsorption site is not blocked by O₂ over these catalysts. Therefore, it is not obvious why such a variation in the catalytic activity is observed over Pd ion substituted Ce_{1-x}M_xO₂ (M = Ti, Zr, Hf).

To understand the activation of lattice oxygen, CO-TPR was carried out in absence of feed oxygen (CO = 0.25 cc min^{-1} ; 275 mg cat; GSHV = $10\,000 \text{ h}^{-1}$; ramp rate = 15 K min^{-1}). Fig. 5 shows the CO oxidation profile over Ce_{0.73}M_{0.25}Pd_{0.02}O_{2- $\delta}$ (M = Ti, Zr and Hf) catalysts in absence of stream oxygen. CO to CO₂ formation occur utilizing lattice oxygen and the reactivity increases in the order Zr < Hf < Ti. This is consistent with the CO oxidation in presence of feed oxygen over the catalyst as shown in Fig. 4(a). Clearly, CO oxidation activity over the corresponding oxides (Fig. 5) without Pd occurs at high temperatures in the almost similar range. On the contrary, CO oxidation over Ce_{0.73}M_{0.25}Pd_{0.02}O_{2- δ} (M = Ti, Zr & Hf) occurs at lower temperatures in absence of feed oxygen. Reactivity increases in the order Zr < Hf < Ti in CeO₂ in presence of Pd.}

3.3.2 Model for CO oxidation. Here we propose a model where CO is adsorbed on the Pd^{2+} site and forms CO₂ utilizing lattice oxygen. The oxide ion vacancy created is refilled by stream oxygen. A bifunctional mechanism can be written as follows:

$$CO(g) + S_{Pd} \rightleftharpoons CO_{ads}$$
 (1)

$$CO_{ads} + O_{L} \rightarrow CO_{2}(g) + \ddot{V}o^{2-} + S_{Pd}$$
⁽²⁾

$$O_2(g) + 2\ddot{V}o^{2-} \rightarrow O_L + O_X$$
(3)

Here O_L is the lattice oxygen and O_X is the dissociated oxygen on intrinsic oxide ion vacancy due to Pd^{2+} ion substitution. O_L and O_X are assumed to be the same kinetically. The rate expression for the above bi-functional mechanism stands as:¹⁶

$$r_{\rm CO_2} = \frac{2K_1k_3k_2C_{\rm CO}C_{\rm O_2}}{K_1k_2C_{\rm CO} + 2k_3C_{\rm O_2}(1 + K_1C_{\rm CO})}$$

where K_1 is the equilibrium constant and k is rate constant of any step.



Fig. 4 (a) %CO₂ formation curve for CO + O₂ reaction (2:2 vol%) over PdO, Ce_{0.98}Pd_{0.02}O_{2-δ}, Ti_{0.99}Pd_{0.01}O_{2-δ}, Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-δ}, Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{2-δ}, Ce_{0.83}Zr_{0.15}Pd_{0.02}O_{2-δ} and Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2-δ} catalysts. (b) Arrhenius plot for CO + O₂ reaction over the Pd substituted catalysts.



Fig. 5 %CO to CO₂ conversion over $Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}$, $Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2-\delta}$ and $Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{2-\delta}$ catalysts and the corresponding oxides without Pd in absence of O₂ (CO = 0.25 cc min⁻¹; 275 mg cat; GSHV = 10 000 h⁻¹; Ramp rate = 15 K min⁻¹).

The experimental data were fitted with this rate equation for Ce_{0.98}Pd_{0.02}O_{2- δ}, Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2- δ}, Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2- δ} and Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{2- δ}. Fig. 6 shows experimental and model fit of the rates of CO oxidation and the values of the optimized rate parameters are given in Table 5. In this model, $K_1 = k_1/k_{-1}$ where the k_1 value is taken from collision theory and k_{-1} , the desorption step is given as $k_{-1} = A \cdot e^{-E/RT}$ as has been reported by Cho.³⁸ So,

Parameter	Value		
$\overline{Ce_{0.08}Pd_{0.02}O_{2.8}}$			
$K_1/\text{cm}^3 \text{ mol}^{-1}$	$3000 \pm 300 \sqrt{T} \exp(1900 \pm 200)/T$		
$k_2 / \text{mol } g^{-1} s^{-1}$	$1.4 \pm 0.2 \times 10^{18} \exp(-21000 \pm 1050)/T$		
$k_3/\text{cm}^3 \text{ g}^{-1} \text{ s}^{-1}$	$3.55 \times 10^{6} \sqrt{T}$		
$Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}$	_		
K_1	$6.1 \pm 07 \ \sqrt{T} \ \exp\left[(17000 \pm 2000)/T\right]$		
k_2	$77.9 \pm 5 \exp \left[(-5700 \pm 100) / T \right]$		
k_3	$3.98 \times 10^{6} \sqrt{T}$		
$Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2-\delta}$	_		
K_1	$2425 \pm 200 \sqrt{T} \exp[(1450 \pm 150)/T]$		
k_2	$1.06 \pm 0.3 \times 10^{16} \exp \left[(-22700 \pm 500) / T \right]$		
k_3	$2.1 \times 10^6 \sqrt{T}$		
$Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{2-\delta}$			
K_1	$6.06 \pm 0.5 \times 10^5 \sqrt{T} \exp \left[(2428 \pm 200)/T \right]$		
k_2	$19 \pm 3 \exp \left[(-5925 \pm 150) / T \right]$		
<i>k</i> ₃	$2.9 \times 10^{6} \sqrt{T}$		



Fig. 6 Experimental and model fitting of the rate of CO oxidation over $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ and $Ce_{0.73}M_{0.25}Pd_{0.02}O_{2-\delta}$ (M = Ti, Zr & Hf).

$$K_{1} = \frac{A_{1}e^{-\frac{E_{1}}{RT}}}{A_{1}e^{-\frac{E_{-1}}{RT}}}$$

where A_1 is proportional to

$$\sqrt{\frac{RT}{2\pi M}}.$$

Therefore,

$$\mathbf{K}_1 = A \sqrt{T} \cdot e \, \frac{-(E_1 - E_{-1})}{R T}$$

For collision, $E_1 \approx 0$, therefore,

$$K_1 = A \cdot e \frac{E_{-1}}{RT}$$

 $\Delta H = E_{-1} - E_1 \approx E_{-1}$. For adsorption, as ΔS is negative, ΔH must be negative to make ΔG negative for chemisorption. In the present catalysts, $-\Delta H/R$ values are 17000, 2428, 1900 and 1450

over $Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}$, $Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{2-\delta}$, $Ce_{0.98}Pd_{0.02}O_{2-\delta}$ and $Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2-\delta}$, respectively.

Activation energy (or E_a/R) for CO₂ formation (k_2) decreases in the order, Ce_{0.73}Zr_{0.25}Pd_{0.02}O_{2- δ} (22700) > Ce_{0.98}Pd_{0.02}O_{2- δ} (21000) > Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{2- δ} (5925) > Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2- δ} (5700). E_a/R value for CO oxidation over various Pd ion substituted catalysts indicates that nature and reactivity of Pd²⁺ ions in different oxide supports.

3.4 XPS studies

Electronic structure of the catalysts can be derived from the XPS core level binding energies of Ce, Ti, Zr, Hf ions in these oxides. Ce(3d) spectra in all the Pd substituted compounds are similar to that of CeO₂ with $3d_{5/2}$ peak at 882.9 eV and the corresponding satellites are at 889 and 899 eV. Ce is in 4+ state in all the compounds. Similarly, Ti(2p_{3/2}) binding energy at 459 eV in both Ti_{0.99}Pd_{0.01}O_{2- δ} and Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2- δ} compounds indicates Ti in 4+ state. Zr(3d) and Hf(4f) ions are also found to be in 4+ state as in ZrO₂ or HfO₂ with binding energies of Zr(3d_{5/2}) at 181.6 and Hf(4f_{7/2}) at 16.7 eV, respectively (not shown).

Electronic states of Pd ion in different support can be extracted from XPS of Pd(3d) core level. Fig. 7(a,b) shows the core level spectra of Pd(3d_{5/2,3/2}) in Pd metal, PdO, Ce_{0.98}Pd_{0.98}O_{2-δ}, $Ce_{0.58}Ti_{0.4}Pd_{0.02}O_{2-\delta}$, $Ce_{1-x-y}Zr_{x}Pd_{y}O_{2-\delta}$ (x = 0.15, 0.25 and 0.4; y = 0.02) and Ce_{0.73}Hf_{0.25}Pd_{0.02}O_{2- δ} and Ti_{0.99}Pd_{0.01}O_{2- δ}. Table 4 shows the binding energy of $Pd(3d_{5/2})$ level in the compounds. The $Pd(3d_{5/2})$ binding energy values are higher than that in PdO at 336.6 eV. Pd(3d_{5/2}) core level binding energy in PdCl₂ is 338.0 eV and $Pd(NO_3)_2$ is 338.2 eV.³⁹ Therefore, Pd is in the +2 state in all the compounds. The core level binding energy gets shifted depending on the effective charge on the metal ion. $Pd(3d_{5/2})$ binding energy in $Ce_{0.98}Pd_{0.98}O_{2-\delta}$ is at 337.7 eV and the value increases to 337.8 eV in $Ce_{0.73}Ti_{0.25}Pd_{0.02}O_{2-\delta}$ and 337.9 eV in $Ti_{0.99}Pd_{0.01}O_{2-\delta}$. Therefore, Pd^{2+} in $Ti_{0.99}Pd_{0.01}O_{2-\delta}$ is highly ionic in nature. However, reverse effect is observed in Pd(3d_{5/2}) binding energy when Zr substitution in CeO_2 was increased from 15 to 40%. The shift in Pd(3d) binding energy toward lower side is clearly observed with Zr substitution (see Fig. 7b). There is a gradual decrease in the $Pd(3d_{5/2})$ binding energy from 337.7 eV in CeO₂ to 337.5 eV in 25% Zr to 337.1 eV in 40% Zr substitution. Interestingly, $Pd(3d_{5/2})$ the binding energy is higher in $Ce_{1-x}Hf_xO_2$ unlike in $Ce_{1-x}Zr_xO_2$. It is at 337.9 eV in $Ce_{0.58}Hf_{0.4}Pd_{0.02}O_{2-\delta}$. Thus, the presence of Ti, Zr and Hf ion in CeO₂ matrix cast different extent of influence on the binding energy/effective charge on Pd ion.

Fig. 8 shows the Pd(3d) core level binding energy region in $Ce_{0.73}M_{0.25}Pd_{0.02}O_{2-\delta}$ (M = Ti, Zr & Hf) reduced at 500 °C for 1 h. Pd(3d_{5/2}) binding energies in the three compounds are at 335.3, 335.2 and 335.3 eV indicating reduction of Pd²⁺ to Pd⁰ state. Therefore, XPS study along with XRD characterization of the reduced sample shows that Pd²⁺ ions occupy the Ce⁴⁺ site in the solid solution and the reduced Pd⁰ atom does not seem to move away from the site. On oxidation in O₂ at 300 °C, Pd⁰ is oxidized to Pd²⁺ state and shifted to the same extent.

Ionic character of Pd^{2+} ion substituted in different reducible oxides can be derived from a plot of effective charge on the Pd ion *vs* core level $Pd(3d_{5/2})$ binding energy shift in PdO, $PdCl_2$ and $Pd(NO_3)_2$ with respect to Pd metal foil. Effective charge is obtained using the equation,



$$1-e^{-\frac{1}{4(\chi_{\rm A}-\chi_{\rm B})}},$$

where χ is the electronegativity of the elements.⁴⁰ Pauling's electronegativity values were used in the calculation of effective charge on Pd ion.¹⁹ Fig. 9(a) shows the plot of effective charge on Pd ion in PdO, PdCl₂ and Pd(NO₃)₂ vs shift in binding energy of Pd(3d_{5/2}) with respect to Pd⁰ in Pd metal. The plot shows a linear dependence of core level binding energy shift with effective charge on Pd ion. From the plot, effective charge on the Pd ions in the Pd ion substituted in the oxides is derived.

The activation energy of CO oxidation over each of the above compounds has been determined (see Table 4) and in Fig. 9(b),



we show a plot of effective charge on Pd ion in each of the above catalysts *vs* activation energy. Clearly, the activation energy decreases with the increase in effective charge on Pd ion. The activation energy decreased from 34 to 13 kcal mol⁻¹.

3.5 Simulations: CO adsorption on ionic Pd

We simulated isolated systems of $(Pd^{\delta+} + CO)$ in order to understand the importance of varying ionicity of Pd ion in different mixed oxide matrices, $Ce_{1-x}M_xO_2$ (M=Ti, Zr, Hf). Table 6 shows the parameters obtained from DFT calculation. The C– O bond is maximally stretched and is the weakest on Pd⁰. As the effective charge on Pd increases, C–O bond length shortens while Pd–C bond length increases. This essentially indicates that σ electron donation (located on C) is enhanced while π back donation from Pd(4d) to CO antibonding orbital is diminished. This is reflected in the depletion of electron density on C and accumulation of the same on Pd ion, as the positive charge on Pd increases. It must be noticed that O atom also get sufficient positive

Table 6 Bond-lengths in the Pd metal/ion + CO systems and net Hirshfeld charge on Pd, C and O obtained from DFT calculation

Pd metal/ion	Pd–C/Å bond length	C–O/Å bond length	Net charge on Pd	Net charge on C	Net charge on O
$\overline{\mathbf{Pd}^0}$	1.790	1.145	0.0597	0.0418	-0.1012
Pd ^{0.5+}	1.827	1.132	0.4024	0.1237	-0.0258
Pd ^{1.0+}	1.859	1.124	0.7236	0.2180	0.0586
Pd ^{1.5+}	1.881	1.118	1.0305	0.3141	0.1555
Pd ^{2.0+}	1.896	1.117	1.3556	0.3944	0.2501



Fig. 9 (a) Plot of effective charge on Pd ion *vs* core level $(3d_{5/2})$ binding energy shift of Pd ion in PdO, PdCl₂ and Pd(NO₃)₂ and the Pd ion substituted oxides. (b) Plot of activation energy of CO oxidation over Pd ion substituted oxides *vs* effective charge on the Pd ion.

charge when Pd has 1.5 or more positive charge which may lead to instability in CO adsorption. From the experiment, we could calculate maximum positive charge on Pd ~ 1 in $Ti_{0.99}Pd_{0.01}O_{2-\delta}$ giving highest CO oxidation activity. In this case, C atom has sufficient positive charge while O atom is just neutral. Pd being the key ion in anchoring adsorbed CO, changes in the effective charge on the Pd ion is therefore important to induce changes in the charge density of C of the adsorbed CO molecule. Our calculations show that the positive charge on carbon atom increases with increasing effective charge on Pd. While stronger binding of CO on to Pd metal would not result in CO oxidation, Pd ion is needed to bind the CO more weakly and also to induce more positive charge on the carbon. So, in the Pd ion substituted $Ce_{1-x}M_xO_2$, depending on the effective positive charge on the Pd ion, oxide ion from lattice would combine to different extent with CO to form CO₂ and hence the difference in the CO oxidation activity.

4. Discussion

When we first proposed $Ce_{1-x}Pd_xO_{2-\delta}$ showing much higher catalytic activity for CO oxidation compared to Pd^0 on CeO_2 or Al_2O_3 , high dispersion of Pd ion acting as an adsorption site was considered as the main reason for high activity.¹³ Subsequent studies on the Pd ion in CeO_2 , TiO_2 , $Ce_{1-x}Ti_xO_2$ oxides showed that CO oxidation activity varied.

To identify the factors responsible for higher catalytic activity over reducible oxides, we chose Pd ion substitution in $Ce_{1-x}M_xO_2$ (M = Ti, Zr, Hf) keeping the parent fluorite structure intact. Advantage with Pd is that it remains in +2 oxidation state. Further, Pd ion is more effective noble metal ion for CO oxidation catalysis than Pt, Rh. Since Zr and Hf ions are not reducible by hydrogen and have similar ionic radii, CO oxidation activity difference is not due to structural modification. Further, H/Pd ratios do not differ much in Ti, Zr and Hf ion substituted compounds.

In ionic reducible oxide catalysts, oxygen is present as oxide ion. That lattice oxide ion react with adsorbed CO molecule is shown experimentally in Fig. 5. If the CO(ads) molecule is polarized at carbon end due to adsorption on Pd²⁺ ion, lattice oxide ion-polarized CO interaction will be ionic in addition to the usual covalent interactions. The primary need is to create noble metal more ionic which can polarize the CO molecule to the maximum positive charge on carbon for nucleophilic attack. Hence ionic interaction between positively polarized CO and negatively charge on Pd ion increases, π back donation from Pd ion to CO antibonding orbital is diminished, thereby facilitating acceptance of electron from nucleophilic oxide ion.

The mechanism of CO oxidation over ionically-substituted noble metal catalysts is shown in Fig. 10 where V_{02-} is the oxide ion vacancy. Thus, the reaction on the ionically substituted catalysts can be written as:

 $CO(adsorbed) + O^{2-} \rightarrow CO_2 + 2e + Vo^{2-}$

 $1/2O_2 + Vo^{2-} + 2e \rightarrow O^{2-}$



Fig. 10 Schematic diagram of CO oxidation mechanism.

From the mechanism, we see Pd^{2+} ion acts as electrophilic site (accept electron from CO) and oxide ion vacancy site as nucleophilic site (donate electron to O_2). Two electrons released by CO are received by Pd^{2+} ion. With increase in the effective charge on Pd ion, greater positive charge is generated on the carbon atom of adsorbed CO molecule making it electron deficient, therefore attack by nucleophilic (negatively charged) lattice oxygen become more favorable.

5. Conclusions

(a) 2 atom% Pd ion substituted $Ce_{1-x}M_xO_2$ (M = Ti, Zr, Hf) have been synthesized by solution combustion method and they crystallize in a fluorite structure.

(b) Activation of lattice oxygen as observed from hydrogen uptake (TPR) studies of $Ce_{1-x}M_xO_2$ (M = Ti, Zr, Hf) oxides is enhanced by the substitution of Pd ion in the lattice.

(c) Effective charge on the Pd ion substituted in CeO₂, $Ce_{1-x}M_xO_2$ (M = Ti, Zr, Hf) and TiO₂ is measured by the Pd(3d) binding energy shifts in the compounds.

is proposed and the model fits well with the experimental observations.

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(d) Activation energy of CO oxidation to CO₂ decreases with

(e) A dual site mechanism with CO and O_2 adsorption on Pd

ion and oxide ion vacancies respectively on the oxide surfaces

increase in the effective charge on Pd ion in these oxides.

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