Enhanced Reducibility of $Ce_{1-x}Ti_xO_2$ Compared to That of CeO_2 and Higher Redox Catalytic Activity of $Ce_{1-x-y}Ti_xPt_yO_{2-\delta}$ Compared to That of $Ce_{1-x}Pt_xO_{2-\delta}$

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Nanocrystalline $Ce_{1-x}Ti_xO_2$ ($0 \le x \le 0.4$) and $Ce_{1-x-y}Ti_xPt_yO_{2-\delta}$ (x = 0.15, y = 0.01, 0.02) solid solutions crystallizing in fluorite structure have been prepared by a single step solution combustion method. Temperature programmed reduction and XPS study of $Ce_{1-x}Ti_xO_2$ (x = 0.0-04) show complete reduction of Ti^{4+} to Ti^{3+} and reduction of $\sim 20\%$ Ce⁴⁺ to Ce³⁺ state compared to 8% Ce⁴⁺ to Ce³⁺ in the case of pure CeO₂ below 675 °C. The substitution of Ti ions in CeO₂ enhances the reducibility of CeO₂. Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta} crystallizes in fluorite structure and Pt is ionically substituted with 2+ and 4+ oxidation states. The H/Pt atomic ratio at 30 °C over Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta} is 5 and that over Ce_{0.99}Pt_{0.01}O_{2-\delta} is 4 against just 0.078 for 8 nm Pt metal particles. Carbon monoxide and hydrocarbon oxidation activity are much higher over Ce_{1-x-y}Ti_xPt_yO₂ (x = 0.15, y = 0.01, 0.02) compared to Ce_{1-x}Pt_xO₂ (x = 0.01, 0.02). Synergistic involvement of Pt²⁺/Pt^o and Ti⁴⁺/Ti³⁺ redox couples in addition to Ce⁴⁺/Ce³⁺ due to the overlap of Pt(5d), Ti(3d), and Ce(4f) bands near E_F is shown to be responsible for improved redox property and higher catalytic activity.

Introduction

Precious metals Pt, Pd, Rh, and Ru are dispersed over an oxide support generally by impregnation, drying, and reduction in hydrogen at ~400-500 °C. The commonly used oxide supports are α -Al₂O₃, γ -Al₂O₃,^{1,2} and SiO₂,³ which are not reducible by hydrogen, and the precious metals disperse as fine metal particles on these supports. On the other hand, CeO₂, TiO₂, and SnO₂ are reducible oxide supports,⁴⁻¹³ and therefore, metals supported on these oxides can become oxidized. Nano-CeO₂ can be partially reduced by hydrogen at $\sim 400-500$ °C to $\text{CeO}_{2-\delta}$ ($\delta \sim 0.1$) and to Ce_2O_3 above 900 °C. Oxygen storage capacity (OSC) was introduced on a quantitative basis, which is the capacity of ceria based support to release oxygen under reducing condition and to uptake oxygen under oxidizing condition.¹⁴ While ZrO₂ cannot be reduced by hydrogen, reducibility of CeO₂ is enhanced in the Ce_{1-x}Zr_xO₂ solid solution, thereby increasing OSC.¹⁵⁻¹⁷ Only the Ce⁴⁺ ion is known to be reduced to a greater extent in the presence of Zr ions. If $Ce_{1-x}Ti_xO_2$ solid solution can be prepared, both Ce and Ti can be reduced and therefore large OSC is expected. Indeed, the formation of $Ce_{1-x}Ti_xO_2$ (x = 0.4) oxides has been reported to be promising toward oxygen storage capacity.18

In an attempt to understand noble metal–CeO₂ interaction, Pd²⁺, Cu²⁺, Pt²⁺, and Rh³⁺ ions were substituted for Ce⁴⁺ in CeO₂ forming a Ce_{1-x}M_xO_{2- δ} solid solution for small values of x = 0.01-0.02.^{19–22} For charge compensation, on lower valent ionic substitution for Ce⁴⁺ in CeO₂, oxide ion vacancies

are created. Enhanced catalytic activity toward CO oxidation, hydrocarbon oxidation, and hydrogen adsorption were observed compared to that of Pt/Al₂O₃ or Pt^o (metal particles) over CeO₂ itself. Synergistic involvement of Pt²⁺/Pt^o and Ce⁴⁺/Ce³⁺ redox couples mediated by oxide ion vacancy is shown to be responsible for higher catalytic activity.²³ Therefore, if Pt²⁺ ions can be substituted for Ce⁴⁺ or Ti⁴⁺ in Ce_{1-x}Ti_xO₂, Pt²⁺/Pt^o along with Ce⁴⁺/Ce³⁺ and Ti⁴⁺/Ti³⁺ redox couples from the support can enhance the redox-catalytic activity further compared to Ce_{1-x}Pt_xO_{2-δ}.

Here we report the redox property of $Ce_{1-x}Ti_xO_2$ (x = 0.1-0.4) in H₂ and a systematic study of the effect of Pt²⁺ substitution in $Ce_{1-x}Ti_xO_2$ forming $Ce_{1-x-y}Ti_xPt_yO_{2-\delta}$ prepared by a single step solution combustion method. Just as the reducibility of $Ce_{1-x}Zr_xO_2$ is higher than that of CeO_2 , $Ce_{1-x}Ti_xO_2$ shows higher reducibility than CeO_2 or TiO₂. Further, $Ce_{1-x-y}Ti_x$ -Pt_yO_{2- δ} showed higher rates of CO, C₂H₂, C₂H₄, and C₃H₈ oxidation activity compared to $Ce_{1-x}Pt_xO_{2-\delta}$.

Experimental Section

TiCl₄ (10 cm³) was added to ice cold (4 °C) acidified water (1 mL of concentrated HCl in 200 mL of H₂O) slowly with continuous stirring forming TiOCl₂. Dilute ammonium hydroxide was added to this solution giving a white precipitate of TiO-(OH)₂. The precipitate was filtered and washed thoroughly to remove chloride ion. Then, TiO(OH)₂ was dissolved in a minimum amount of concentrated nitric acid to obtain the nitrate precursor TiO(NO₃)₂. The Ti ion concentration in the solution was estimated by the colorimetric method.²⁴

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 $Ce_{1-x}Ti_xO_2$ (x = 0.1-0.4) were prepared by taking stoichiometric amounts of $(NH_4)_2Ce(NO_3)_6\cdot 6H_2O$ (E. Mark India Ltd.), TiO(NO₃)₂, and glycene and heating at 400 °C to give a flaming combustion.^{25,26}

Reducibility of Ce_{1-x}Ti_xO₂ Compared to That of CeO₂

Chemical reactions occurring in the combustion process can be written as follows:

$$3(NH_4)_2Ce(NO_3)_6 + 8C_2H_5NO_2 \rightarrow$$

 $3CeO_2 + 10N_2 + 16CO_2 + 32H_2O$ (1)

$$9\text{TiO}(\text{NO}_3)_2 + 10\text{C}_2\text{H}_5\text{NO}_2 \rightarrow$$

 $9\text{TiO}_2 + 14\text{N}_2 + 20\text{CO}_2 + 25\text{H}_2\text{O}$ (2)

$$9(1 - x)(NH_4)_2Ce(NO_3)_6 + 9xTiO(NO_3)_2 + 10C_2H_5NO_2 + 14(1 - x) C_2H_5NO_2 \rightarrow 9Ce_{1-x}Ti_xO_2 + 20CO_2 + 28(1 - x)CO_2 + 14N_2 + 34(1 - x)N_2 + 25H_2O + 71(1 - x)H_2O (3)$$

Pt/Ce_{0.85}Ti_{0.15}O₂ (1 atom %) was prepared by the solution combustion method taking (NH₄)₂Ce(NO₃)₆•6H₂O, Pt(NH₃)₄-(NO₃)₂ (ABCR, France), TiO(NO₃)₂, and glycene in the mole ratio of 0.8415:0.01:0.1485:2.42. In a typical preparation, 3 g of (NH₄)₂Ce(NO₃)₆•6H₂O, 0.0252 g of Pt(NH₃)₄(NO₃)₂, 0.1823 g of TiO(NO₃)₂ (in solution), and 1.1814 g of glycine were taken in a 300 mL Pyrex dish. Similarly, 2 atom % Pt/Ce_{0.85}Ti_{0.15}O₂ was also prepared. To compare the catalytic activity of 1 atom % Pt impregnated over combustion, synthesized Ce_{0.85}Ti_{0.15}O₂ was prepared by reducing H₂PtCl₆ dispersed over the oxide support by hydrazine.

X-ray diffraction (XRD) data of all the mixed oxides and the Pt-substituted oxides were recorded on a SIEMENS D5005 diffractometer at a scan rate of 0.5° min⁻¹ in the 2θ range between 20° and 100°. For the structural refinement by the Rietveld method, the XRD data were recorded in a Philips X'Pert diffractometer at a scan rate of 0.5° min⁻¹ with a 0.02° step size in the 2θ range between 20° and 100°. The refinement was done with the FullProf-fp2k program²⁷ varying 17 parameters simultaneously.

X-ray photoelectron spectra (XPS) of the prepared samples and a few hydrogen reduced materials were recorded in an ESCA-3 Mark II spectrometer (VG Scientific Ltd., England), using Al K α radiation (1486.6 eV). Binding energies were calibrated with respect to C(1s) at 285 eV with a precision of ± 0.2 eV. For XPS analysis the powder samples were made into 0.5 mm thick, 8 mm diameter pallets and placed into an ultrahigh vacuum (UHV) chamber at 10⁻⁹ Torr housing the analyzer. The obtained spectra were curve fitted with Gaussian peaks after subtracting a linear background.

Hydrogen Uptake Measurement and Catalytic Reactions

Hydrogen uptake measurements were performed in a continuous flow microreactor of length 30 and 0.4 cm internal diameter with 5.49% H₂/Ar (certified calibration gas mixture from Bhuruka Gases Ltd., Bangalore) flowing at 30 sccm at a linear heating rate of 10 deg min⁻¹ up to 700 °C. For Pt-substituted samples, the low temperature was achieved through liquid nitrogen cooling. Hydrogen concentration was monitored by a thermal conductivity detector (TCD). The volume of hydrogen consumed was calibrated against the reduction of a known amount of CuO. The gas flow was monitored with a mass flow sensor (AWM3100V) calibrated with a standard bubble flow meter. Hydrogen uptake over Pt-substituted samples also has been carried out under isothermal condition.

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 (dimensions 25



Figure 1. (a) Percent CO conversion as a function of temperature over $Ce_{0.85}Ti_{0.15}O_2$, and Pt, Ti substituted oxides under the following reaction conditions: CO = 2 vol %, $O_2 = 2$ vol %, $F_t = 100$ sccm, $GHSV = 43\ 000\ h^{-1}$, W = 25 mg.

cm × 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 obtain a column length of 1.1 cm and the ends 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. Actual rates of the reactions were obtained following the percent conversion as a function of *W/F*, where *W* is the weight of the catalyst and *F* is the gas flow rate in moles/second. Before the catalytic test, the as-prepared catalyst was heated in O₂ flow at 200 °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 10 deg min⁻¹.

Results

Catalytic Test. CO oxidation over the catalysts are carried out with 25 mg of each catalyst at space velocity of 43 000 h⁻¹ with 2:2 vol % of CO and O2. The heating rate was also kept constant at 10 deg/min. In Figure 1, CO conversion vs temperature plots are shown. As can be seen from the figure, $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$ catalyst has a much lower light-off temperature with $T_{50} = 170$ °C compared to Ce_{0.99}Pt_{0.01}O_{2- δ} with $T_{50} = 260$ °C. Further, T_{50} of 2 atom % Pt in CeO₂ or Ce_{0.85}-Ti_{0.15}O₂ are lower compared to the corresponding 1 atom % Pt oxides. A 1 atom % Pt metal impregnated catalyst over Ce_{0.85}-Ti_{0.15}O₂ shows T₅₀ of 260 °C compared to 170 °C in the combustion synthesized catalyst. Having observed higher catalytic activity from the light-off curves for Pt in $Ce_{1-x}Ti_xO_2$ compared to Pt in CeO₂, actual rates were estimated by running the reactor under differential condition: rate = $F_{CO}x/W$, where $F_{\rm CO}$ in the molar flow rate (moles/second), W is the weight of the catalyst (grams), and x is the fractional conversion. A series of reactions were carried out by varying W keeping the CO:O₂ ratio of 2:6 vol % constant. Total gas flow was kept constant at 100 sccm made up with He. Space velocity was kept constant at 43 000 h⁻¹. In Figure 2a, fractional CO conversion vs W/Fplots is shown at various temparatures. From the figure it can be noted that even up to 40% conversion, x vs W/F is linear. Accordingly, from the slopes, rates were estimated. CO oxidation experiments were carried out over $Ce_{0.99}Pt_{0.01}O_{2-\delta}$ under the same experimental conditions, and here also up to 40% conversion, conversion was linear with W/F. In Figure 2b rates of CO conversion (μ mol·gm⁻¹·s⁻¹) vs temperature are plotted. Clearly, there is a huge difference in the CO oxidation rates between Pt in $Ce_{1-x}Ti_xO_2$ and Pt in CeO₂. At 155 °C, the rate of CO conversion over $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$ is 45 times higher



Figure 2. (a) *x* vs W/F_{CO} plot of Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2 $-\delta$}. (b) Rate vs temperature from a *W*/F_{CO} plot and the light-off curve for Ce_{0.99}Pt_{0.01}O_{2 $-\delta$} and Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2 $-\delta$}.

than that over $Ce_{0.99}Pt_{0.01}O_{2-\delta}$. In the same plot, rates derived from light-off curves taking conversion up to 25% are plotted for the two catalysts. The rates obtained from the light-off curve below 15% conversion are in good agreement with the rates obtained under differential condition. Further, the conversion up to 15% is linear with *W* up to 150 mg of catalyst. Therefore, rates of CO oxidation as a function of P_{O_2} , rates of hydrocarbon oxidation, and NO reduction reported here are taken for conversions less than 15% by running the reaction with 100– 150 mg of the catalyst with GHSV of 43 000h⁻¹.

In Figure 3a, activation energy of CO oxidation is given taking rates from W/F plots and activation energy is 13.2 kcal/mol with Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2- δ}, and it is much lower than that over Ce_{0.99}Pt_{0.01}O_{2- δ} with a value of 19.6 kcal/mol. Thus, Ce_{1-x}Ti_xO₂ is a better oxide support for Pt than pure CeO₂.

Partial pressure dependence of oxygen over CO oxidation is shown in Figure 3b where 2 vol % of CO is kept constant and the volume percent of oxygen was varied from 0.2 to 10. Reaction was carried out with 50 mg of $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$ catalyst. From the log(rate) vs log(P_{O_2}), we find that when the partial pressure of oxygen is lower than the of CO, the order is 0.78 and in excess oxygen condition, the order is 0.28.

In Figure 4a light-off curves of C_2H_2 , C_2H_4 , and C_3H_8 oxidation over 100 mg of the two catalysts are given. In each of the reactions, 1 vol % of "HC" was taken and the "HC" to oxygen ratio was 1:5 with a total flow of 100 sccm. In Figure 4b, Arrhenius plots are given for all the reactions with the two catalysts taking the rates estimated below 15% conversion. Clearly, $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$ shows higher catalytic activity compared to $Ce_{0.99}Pt_{0.01}O_{2-\delta}$. The activation energies are lower for the $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$ compared to $Ce_{0.99}Pt_{0.01}O_{2-\delta}$ for oxidation of all the hydrocarbons studied here.

NO reduction by CO was carried out taking 0.25 vol % of NO and 0.25 vol % of CO with a 40 sccm total flow over 150



Figure 3. (a) Arhenious plot [In(TOF) vs 1/*T*] for CO oxidation over $Ce_{0.99}Pt_{0.01}O_{2-\delta}$ and $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$. (b) Rate vs O₂ partial pressure dependence over $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$.

mg of catalysts and in Figure 5, the percent NO conversion vs temperature is given. NO reduction activity over Ce_{0.84}Ti_{0.15}-Pt_{0.01}O_{2- δ} and Ce_{0.99}Pt_{0.01}O_{2- δ} is similar. The rate of conversion at 135 °C (at 15% conversion) is 2 × 10⁻⁷ mol gm⁻¹ s⁻¹. Activation energies are 23 and 24 kcal mol⁻¹ for Ce_{0.99}Pt_{0.01}O_{2- δ} and Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2- δ}, respectively.

Hydrogen Uptake Studies. Figure 6a shows the temperature programmed reduction profiles of $Ce_{1-x}Ti_xO_2$ (x = 0.0-0.4) along with pure TiO_2 . Notice the Y-scales are different in the plots for different compositions. Pure CeO₂ shows H₂ uptake from 350 °C with a low-temperature peak at \sim 500 °C, which has been attributed to surface cerium reduction¹⁴ followed by bulk cerium reduction beyond 550 °C. The area under the peak up to 675 °C corresponds to 5.2 cm³ of H₂ per g of CeO₂. Upon Ti substitution, the reduction starts at \sim 300 °C. The total reduction up to 675 °C has been evaluated for all the compositions and the data are given in Table 1. Clearly, the extent of reduction increases with increase in Ti content. The samples were reoxidized by passing oxygen at 300 °C for 1 h. The hydrogen uptake of the reoxidized sample in the subsequent cycle was about the same as that in the first cycle. From the volume of hydrogen taken up by Ce_{0.6}Ti_{0.4}O₂ up to 675 °C, the stoichiometry of the reduced oxide is $Ce_{0.46}^{+4}Ce_{0.14}^{+3}Ti_{0.4}^{+3}O_{1.73}^{-1.73}$, on the basis of 100% reduction of Ti⁴⁺ to the Ti³⁺ state. That the Ti⁴⁺ ion is fully reduced to Ti³⁺ in the TPR is substantiated by XPS studies presented later. While only 16% Ti is reduced from Ti^{4+} to Ti^{3+} up to 675 °C in TiO_2 , 100% Ti from Ti^{4+} is reduced to 3+ in the solid solution. Only about 8% Ce is reduced in pure CeO₂ up to 675 °C but over 20% Ce⁴⁺ is reduced in $Ce_{1-x}Ti_xO_2$. Thus, reducibility of both Ce^{4+} and Ti^{4+} is enhanced in $Ce_{1-x}Ti_xO_2$.

Figure 6b shows the TPR profiles of 1-2 atom % Pt/Ce_{0.85}-Ti_{0.15}O₂ from -100 to 650 °C. There are three regions of



Figure 4. (a) Percent CO₂ formation as a function of temperature for different hydrocarbon oxidation over Ce_{0.99}Pt_{0.01}O_{2- δ} and Ce_{0.84}Ti_{0.15}-Pt_{0.01}O_{2- δ}. Reaction conditions: "HC" = 1 vol %, O₂ = 5 vol %, *F*_t = 100 sccm, GHSV = 43 000 h⁻¹, *W* = 100 mg. (b) Arrhenius plot [ln-(rate) vs 1/*T*] for corresponding hydrocarbon oxidation as in part a.



Figure 5. Percent NO conversion vs temperature for the reaction NO + CO under the following conditions: NO = 0.25 vol %, CO = 0.25 vol %, $F_t = 40$ sccm, GHSV= 20 000 h⁻¹, W = 150 mg.

hydrogen uptake: first one extends from -50 to 120 °C; the second region extends from \sim 120 to 300 °C; and the third region is above 300 °C. The low-temperature region corresponds to hydrogen uptake related to Pt species in the compound.²³ The second and the third regions of the H₂ uptake can be attributed to the reduction of the Ti⁴⁺ and the Ce⁴⁺ state, respectively. Reduction of both Ti⁴⁺ and Ce⁴⁺ ions occurs at a lower temperature upon Pt substitution and the extent of reduction of Ce⁴⁺ is increased. The H₂ uptake curve for Ce_{0.99}Pt_{0.01}O_{2- δ} is also given for comparison in the figure. The H₂/Pt molar ratio in the first region of 1 atom % Pt/Ce_{0.85}Ti_{0.15}O₂ is 12.0, which is 3 times higher than that observed over 1 atom % Pt/CeO₂.²³ For 2 atom % Pt/Ce_{0.85}Ti_{0.15}O₂, the ratio is 7.5 under region 1. Total H₂ uptake up to 650 °C is also much higher than that of the corresponding Ce_{1-x}Ti_xO₂ oxides without Pt. The reduced



Figure 6. (a) TPR profiles of pure CeO₂ (curve A), Ce_{1-x}Ti_xO₂ (x = 01-0.4) (curves B, C, D, E) solid solutions, and pure TiO₂ (curve F); (b) TPR profile of Ce_{0.99}Pt_{0.01}O_{2- δ} (curve A), Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2- δ} (curve B), Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2- δ} (curve C), and Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2- δ} (curve C', cycle-2). Notice the difference in the *Y*-scale for different samples.

TABLE 1: Rietveld Refined Parameters for CeO₂, $Ce_{1-x}Ti_xO_2$ (x = 0.0-0.4) Compounds

compd	$R_{\rm Bragg}$	$R_{\rm F}$	$R_{\rm P}$	χ^2	a (Å)
CeO ₂	1.17	0.90	6.00	1.02	5.4131(6)
Ce _{0.9} Ti _{0.1} O ₂	1.58	0.98	5.16	1.10	5.4061(6)
Ce _{0.85} Ti _{0.15} O ₂	1.01	1.01	6.06	1.16	5.4032(2)
Ce _{0.8} Ti _{0.2} O ₂	2.45	1.81	7.06	1.04	5.3989(2)
Ce _{0.7} Ti _{0.3} O ₂	1.77	1.25	5.25	1.09	5.3892(5)
Ce _{0.6} Ti _{0.4} O ₂	1.98	1.32	5.65	1.11	5.3720(3)

material is oxidized when exposed to air even at room temperature, as observed from the amount of hydrogen taken up by the reduced sample exposed to air. After the first cycle, O_2 was passed at 300 °C for 1 h followed by purging with pure Ar and a second TPR run was carried out. The H₂ uptake curves in the second cycle were similar to those in the first cycle [compare curves C and C' of Figure 6b].

The H₂ uptake experiment was also carried out under isothermal condition at 30 °C as a function of time. The experiment was repeated for reduction-oxidation cycles at 30 °C to check for the reversibility of H₂ uptake. First, H₂ uptake was measured at 30 °C over 1 atom % Pt/Ce_{0.85}Ti_{0.15}O₂. When O2 was passed at 30 °C over the H2 adsorbed catalysts, temperature increased to 38 °C indicating $H_2 + O_2$ to H_2O reaction. The reactor was purged with pure Ar and again H₂/Ar was passed. Adsorption of H_2 followed by the $H_2 + O_2$ reaction cycle was repeated over 50 times and each time the volume of H₂ adsorbed was the same (Figure S1, Supporting Information). However, the H₂ adsorbed sample was purged with Ar and a repeat H₂/Ar run did not show any H₂ uptake. The H₂/Pt molar ratios were 2.5 and 1.5 for 1 and 2 atom % Pt in Ce_{0.85}Ti_{0.15}O₂. The H₂/Pt molar ratio at 30 °C for $Ce_{0.99}Pt_{0.01}O_{2-\delta}$ was 2. This means for 1 atom % $Pt/Ce_{0.85}Ti_{0.15}O_2$ the number of H atoms per Pt atom adsorbed at 30 °C is 5. The H₂ adsorption was carried out at 30 °C over ~80 Å Pt metal particles (prepared by the polyol reduction method) in a separate experiment. The H₂/Pt molar ratio was 0.078. Thus, at 30 °C, there is 25 times enhancement of H₂/Pt over Ce_{0.99}Pt_{0.01}O_{2- δ} and 32 times over $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$ compared to Pt metal particles. The number of H atoms per surface Pt atom (estimated from ~80 Å Pt metal particles) turnes out to be 0.97, which is close to 1. This is what is expected for Pt metal particles. To confirm whether the adsorbed H₂ reacts with O₂ at 30 °C, O₂ was passed over the H₂ adsorbed catalyst in the catalytic reactor equipped with QMS. First H₂/He was passed over 1 atom % Pt/Ce_{0.85}Ti_{0.15}O₂, the



Figure 7. (a) XRD patterns of (A) CeO₂, (B) CeO₂ $(Ti_{0.1}O_2, (C) CeO_8Ti_{0.2}O_2, (D) CeO_7Ti_{0.3}O_2, (E) CeO_6Ti_{0.4}O_2, and (F) CeO_5Ti_{0.5}O_2$. The asterisk indicates the anatase TiO₂ 100% peak. (b) Rietveld refined observed (\bigcirc), calculated (+), and difference XRD patterns of CeO₆Ti_{0.4}O₂.

sample was purged with He, and then O₂/He was passed over the catalyst. Formation of H₂O is detected by the mass spectrometer. When H₂/He and O₂/He are passed simultaneously, H₂O is formed at 30 °C, but the temperature increased rapidly due to the exothermic nature of the reaction H₂ + O₂ \rightarrow H₂O. This clearly suggests that the H₂ adsorbed is either dissociated or a precursor for dissociation. Thus, the isothermal H₂ uptake experiment also shows higher H₂ uptake for Pt in Ce_{0.85}Ti_{0.15}O₂ than Pt in CeO₂. Enhanced reducibility of CeO₂ due to Ti ion substitution by hydrogen in both the presence and the absence of Pt and enhanced catalytic activity of Ce_{1-x-y}Ti_xPt_yO_{2- δ} compared to Ce_{1-x}Pt_xO_{2- δ} is to be attributed to the structure of Ce_{1-x}Ti_xO₂ and Pt/Ce_{1-x}Ti_xO₂. Therefore, a detailed study of the structure of the oxides was undertaken.

XRD Studies. Figure 7a shows the XRD pattern of $Ce_{1-x}Ti_xO_2$ for x = 0.0-0.5. All the XRD patterns can be indexed to the

fluorite structure. Peaks due to TiO₂ in anatase or rutile phases are not detectable up to x = 0.4 even when the pattern is expanded in the *Y*-scale. For x = 0.5, the TiO₂ (110) peak is visible. There is a systematic increase in the 2θ values of the diffraction lines with the increase in Ti indicative of solid solution formation. The background is flat for $2\theta = 20-90^\circ$, indicating the material is crystalline. The line width increased with increasing Ti_x for x = 0.2, which further supports the idea of solid solution. To confirm further, Rietveld refinements were carried out while simultaneously varying 17 parameters such as overall scale factor and background parameter. Observed, calculated, and difference plots are given for the x = 0.4 sample in Figure 7b (see Figure S2, Supporting Information, for x =0.1 composition). The structural parameters are given in Table 2. Lattice parameter "a" decreased from 5.4131(6) Å for CeO₂

TABLE 2: Composition of CeO₂, Ce_{1-x}Ti_xO₂, and Ce_{1-x}-yTi_xPt_yO_{2- δ} Compounds Reduced by Hydrogen up to 675 °C

compd	H_2 uptake up to 675 °C, mol/g (×10 ⁻⁴)	formula of the reduced species	% Ce ⁴⁺ reduced to Ce ³⁺
CeO ₂	2.3	CeO _{1.96}	8
TiO ₂	10.0	TiO _{1.92}	
Ce _{0.9} Ti _{0.1} O ₂	7.4	Ce _{0.9} Ti _{0.1} O _{1.88}	15.5
Ce _{0.85} Ti _{0.15} O ₂	8.8	Ce _{0.85} Ti _{0.15} O _{1.86}	15
Ce _{0.8} Ti _{0.2} O ₂	11.1	Ce _{0.8} Ti _{0.2} O _{1.83}	17.5
Ce _{0.7} Ti _{0.4} O ₂	15.9	Ce _{0.7} Ti _{0.3} O _{1.77}	22
Ce _{0.6} Ti _{0.4} O ₂	20.0	Ce _{0.6} Ti _{0.4} O _{1.73}	23.5
$Ce_{0.99}Pt_{0.01}O_{2-\delta}$	2.9	Ce _{0.99} Pt _{0.01} O _{1.95}	10
Ce _{0.84} Ti _{0.15} Pt _{0.01} O _{2-δ}	15.7	Ce _{0.84} Ti _{0.15} Pt _{0.01} O _{1.75}	36
$Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2-\delta}$	23.2	$Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{1.63}$	60

to 5.3720(3) for x = 0.4. A systematic decrease in the lattice parameter confirms Ce_{1-x}Ti_xO₂ solid solution formation.

In Figure 8a-c, XRD patterns of 1 atom % Pt in Ce_{0.85}-Ti_{0.15}O₂ made by the combustion method and 1 atom % Pt impregnated over combustion synthesized Ce_{0.85}Ti_{0.15}O₂ are shown by expanding the Y-scale 25 times after normalizing the intensities with respect to the (111) peak. The position of the 100% peak expected due to anatase TiO₂ at $2\theta = 25.3^{\circ}$ [marked arrow in Figure 8a] is absent in the pattern even at an expansion of 25 times in the Y-scale. The Pt(111) peak is to be observed at $2\theta = 39.8^{\circ}$ and expansion of the curve in Figure 8b shows that the intensity in the Pt(111) peak region is negligibly small; it is in the noise level. But a good Pt(111) peak is observed for the Pt/Ce_{0.85}Ti_{0.15}O₂ impregnated sample (Figure 8c). Pt in H₂-PtCl₆ taken in the combustion synthesis is converted into Pt°, PtO, or PtO₂; at least 100% intensity peak due to these oxides should be of detectable intensity as in the Pt/Ce_{0.85}Ti_{0.15}O₂ (impregnated) sample, but no such peak could be detected. Therefore, Pt is finely dispersed as either atoms or ions. As is shown later, Pt is dispersed as ions from XPS studies. Therefore, the natural position for the Pt ions in CeO_2 is the Ce^{4+} site. The structure of $Ce_{0.99}Pt_{0.01}O_{2-\delta}$ by EXAFS indeed showed Pt^{2+} ion substitution for Ce4+ in CeO2 where a unique Pt-Ce distance is obtained at 3.28 Å.21 Rietveld refinement of XRD profiles of $Ce_{0.85}Ti_{0.15}O_2$ and $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$ was done (see Figure S3a,b, Supporting Information, for 1% and 2% Pt in $Ce_{0.85}Ti_{0.15}O_2$) and lattice parameter "a" is 5.4032(2) and 5.4052-(3) Å, respectively. The increase in the lattice parameter is significant, which indicates Pt ionic substitution in $Ce_{1-x}Ti_xO_2$.

High-Resolution TEM Study. The high-resolution TEM image and the electron diffraction pattern of combustion synthesized $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$ are shown in Figure 9, parts a and b, respectively. The fringes spaced at \sim 3.20 Å correspond to CeO₂(111) layers. Fringes due to Pt metal particles separated at 2.30 Å are absent. The electron diffraction pattern clearly shows the fluorite structure of the compound. No spot or ring due to Pt metal is detectable. The average particle size is ~ 150 Å, which agrees well with that calculated from X-ray diffraction with use of the Scherrer formula. EDAX analysis on these images showed a Pt:Ti:Ce ratio close to 76:23:1 as shown in Figure 9c, which is close to the bulk composition within the experimental error. In Figure 9d the high-resolution TEM image of Pt metal impregnated over Ce_{0.85}Ti_{0.15}O₂ is shown. Clearly, Pt metal particles with Pt(111) fringes at 2.30 Å are observed and are marked in the figure. The lattice fringes with 3.20 Å are due to Ce_{0.85}Ti_{0.15}O₂. Thus, the HRTEM study confirmed the presence of Pt metal particles in the Pt impregnated over $Ce_{0.85}Ti_{0.15}O_2$. Therefore, the absence of Pt metal particles in the TEM image and the presence of Pt X-ray emission on the



Figure 8. XRD patterns of (a) $Ce_{0.85}Ti_{0.15}O_2$, (b) $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$, and (c) 1 atom % Pt impregnated $Ce_{0.85}Ti_{0.15}O_2$ (all the curves were magnified by 25 times in the *Y*-scale).

high-resolution image confirm Pt ion substitution in the combustion synthesized $Pt/Ce_{0.85}Ti_{0.15}O_2$.

XPS Studies. To gain confidence in the XPS of Pt metal peaks vs oxidized Pt in CeO2, Pt(4f) of Pt metal foil in metallic contact with the XPS probe, a Pt metal foil insulated from the XPS probe by the ZrO₂ pallet were recorded. In addition, Pt metal particles made into a pallet in contact with the probe, Pt metal impregnated over Ce_{0.85}Ti_{0.15}O₂, (NH₃)₄Pt^{II}(NO₃)₂, and PtO_2 (in the form of compact 1 mm thick pallets), were also recorded. Pt metal foil and Pt metal particles did not show any charging. Pt(4f) peaks from Pt metal foil that was insulated over the ZrO₂ pallet showed a charging shift of 2.6 eV. Pt metal impregnated over Ce_{0.85}Ti_{0.15}O₂ showed a charging shift of 6.4 eV. The $Ce_{0.99}Pt_{0.01}O_{2-\delta}$ pallet showed charging of 6.3 eV. Correction for the shift due to charging was done taking C(1s) at 285 eV; since compact pallets are used for powder samples, there is no differential charging. In Figure 10a, Pt(4f) of the above samples are shown. $Pt(4f_{7/2,5/2})$ peaks due to Pt metal foil with no charging shift and with a charging shift after correction overlap fully with binding energies at 71.1 and 74.2 eV. There is no measurable increase in the width of the Pt(4f) peaks due to charging. Pt(4f) peaks from the Pt metal impregnated sample show an indication of surface oxidation from the decrease in $4f_{7/2.5/2}$ peak resolution, even though the main peaks are due to Pt in the metallic state. The binding energy of $Pt^{2+}(4f_{7/2,5/2})$ from (NH₃)₄Pt^{II}(NO₃)₂ is at 72.4 and 75.6 eV (curve D, Figure 10). Thus, filling up the valley between $(4f_{7/2,5/2})$ peaks in Pt metal impregnated over Ce_{0.85}Ti_{0.15}O₂ (curve C, Figure 10) is due to surface oxidation of Pt° to the Pt²⁺ state. In curve E in Figure 10, the Pt(4f) peak from α -PtO₂ is plotted where Pt is in the 4+ state. In this compound, there was no charging shift because it is a conducting oxide. Binding energies of $Pt(4f_{7/2,5/2})$ are at 75.0 and 78.2 eV, respectively. The Pt(4f) spectrum from $Ce_{0.99}Pt_{0.01}O_{2-\delta}$ is distinctly different and indicative of oxidized Pt with more than one oxidation state as seen from Figure 10b. Under such condition, it is common to resolve the spin-orbit doublets into components due to different oxidation states. Accordingly, the $Ce_{0.99}Pt_{0.01}O_{2-\delta}$ is deconvoluted into sets of Pt(4f_{7/2,5/2}) spin-orbit doublets taking into account fwhm from Pt metal 4f7/2,5/2 states, spin-orbit splitting of 3.2 eV, and relative intensity of $7/_2$ and $5/_2$ states. The Pt(4f) spectrum of $Ce_{0.99}Pt_{0.01}O_{2-\delta}$ deconvoluted into three sets of spin-orbit states is shown in Figure 10b. The $Pt(4f_{7/2})$ peaks at 71.1, 72.4, and



Figure 9. (a) HRTEM image, (b) the corresponding ED pattern, (c) EDAX of $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_2$, and (d) HRTEM image of 1 atom % Pt impregnated over $Ce_{0.85}Ti_{0.15}O_2$.

75 eV coincide with model compounds with Pt in 0, 2+, and 4+ oxidation states. If the peak due to Pt° is not taken into account, fwhm becomes too high for Pt^{2+} and Pt^{4+} , which is not realistic.

In the XPS study of the Pt(4f) core level spectrum in $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$, the Pt(4f) was deconvoluted into two sets of spin-orbit doublets, since intensity due to Pt° is not observed. Accordingly, the Pt(4f_{7/2,5/2}) peaks at 72.6, 75.8 and 75.0, 78.2 eV are due to Pt in 2+ and 4+ oxidation states, respectively (Figure 11a). In $Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2-\delta}$ (Figure 11b), the $Pt(4f_{7/2,5/2})$ region was deconvoluted into three sets of spin-orbit doublets since the intensity due to Pt° was significant. Accordingly, $Pt(4f_{7/2})$ peaks at 71.1, 72.7, and 74.9 eV are assigned to Pt° , Pt²⁺, and Pt⁴⁺ oxidation states, respectively. The Ce_{0.83}Ti_{0.15}- $Pt_{0.02}O_{2-\delta}$ was reduced in a tubular furnace in H₂ at 675 °C for 6 h and the XPS of the reduced sample showed a much higher intensity of the Pt° state (Figure 11c). The same sample upon air oxidation at 500 °C shows peak positions and intensities due to Pt°, Pt²⁺, and Pt⁴⁺ as in the "as-prepared" sample (Figure 11d). In Table 3 the binding energies of $Pt(4f_{7/2})$ in the model compounds and the catalysts, full width at half-maximum (fwhm) of the $4f_{7/2}$ peak, and relative intensities of Pt^o, Pt²⁺, and Pt4+ states calculated from the respective areas are

presented. In Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2- δ}, 63% Pt is in the 2+ state and 37% in the 4+ state. For 2 atom % Pt-substituted sample, about 7% Pt is found in the Pt^o state and 65% Pt in the Pt²⁺ state. In the H₂-reduced sample, the peak intensity at 71.1 eV due to Pt^o is 49% and that of Pt²⁺ is 45%. There is a decrease in the Pt⁴⁺ peak intensity and an increase in the Pt^o state upon H₂ reduction in the reduced sample. Peaks due to the Pt²⁺ state persist. Ce_{0.83}Ti_{0.15} Pt_{0.02}O_{2- δ} upon hydrogen reduction turns black. The sample upon exposure to air even at room temperature changes to gray, which is the same color as the "asprepared" sample. Thus, in combustion synthesized 1 and 2 atom % Pt/Ce_{0.85}Ti_{0.15}O₂, Pt is present mainly in the 2+ state.

The surface concentration of Pt in all the as-prepared samples was calculated employing the following equation: 28

$$\frac{X_{\rm Pt}}{X_{\rm (Ce+Ti)}} = \frac{I_{\rm Pt}(\sigma_{\rm Ce}\lambda_{\rm Ce} + \sigma_{\rm Ti}\lambda_{\rm Ti})}{(I_{\rm Ce} + I_{\rm Ti})\sigma_{\rm Pt}\lambda_{\rm Pt}}$$
(4)

where *X*, *I*, σ , λ , and D_E are the surface concentration, intensity, photoionization cross-section, mean escape depth, and geometric factors, respectively. The integrated area under the respective core level peak after subtracting a linear background was taken as the measure of observed intensity. The photoionization cross-



Figure 10. (a) XPS of the Pt(4f) core level in (A) Pt metal foil in contact with the XPS probe, (B) Pt metal foil over the insulating ZrO_2 pallet, (C) 1 atom % Pt impregnated over $Ce_{0.85}Ti_{0.15}O_2$, (D) (NH₃)₄-Pt^{II}(NO₃)₂, and (E) PtO₂. (b) XPS of the Pt(4f) spectrum of $Ce_{0.99}Pt_{0.01}O_{2-\delta}$ deconvoluted into Pt^o, Pt²⁺, and Pt⁴⁺ states.

sections and mean escape depth were taken from the literature.^{29,30} The surface concentrations of Pt in the as-prepared 1 and 2 atom % Pt/Ce_{0.85}Ti_{0.15}O₂ are 3.5% and 4.0%, respectively. Thus, the surface concentration of Pt is higher than that in the bulk, indicating significant surface segregation of platinum in the as-prepared samples. Surface concentration of Ti in Ce_{1-x}Ti_xO₂ was close to the bulk composition within experimental error of $\pm 3\%$ and no surface segregation of Ti is observed.

The Ti(2p) spectra of pure TiO₂, Ce_{0.6}Ti_{0.4}O₂, Ce_{0.6}Ti_{0.4}O_{1.73} (reduced up to 675 °C in the TPR), as-prepared 1 to 2 atom % Pt/Ce_{0.85}Ti_{0.15}O₂, and 2 atom % Pt/Ce_{0.85}Ti_{0.15}O₂ (reduced up

TABLE 3: Binding Energies of Pt(4f_{7/2}), Relative Intensity, and fwhms of Different Pt-Substituted Samples

catalyst	species	binding energy of Pt4f _{7/2} (eV)	rel intensity (%)	fwhm (eV)
Pt metal	Pt°	71.1		2.2
$(NH_3)_4Pt^{II}(NO_3)_2$	Pt^{2+}	72.4		2.4
α -PtO ₂	Pt^{4+}	75		2.4
$Ce_{0.99}Pt_{0.01}O_{2-\delta}$	Pt°	71.0	7	2.4
	Pt^{2+}	72.3	71	2.8
	Pt^{4+}	74.5	22	2.9
$Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$	Pt°			
	Pt^{2+}	72.6	62.7	2.7
	Pt^{4+}	75	37.3	3.0
Ce_0.83Ti_0.15Pt_0.02O_2-\delta	Pt°	71.1	7.6	2.2
	Pt^{2+}	72.7	67.1	2.7
	Pt^{4+}	74.9	25.3	2.9
$Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2-\delta}$	Pt°	71.1	49.0	2.2
(reduced at 675 °C	Pt^{2+}	72.6	45.0	2.7
for 6 h)	Pt ⁴	74.8	7.0	2.9
Ce0.83Ti0.15Pt0.02O2-0	Pt°	71.0	12.4	2.2
(reoxidized in air at	Pt^{2+}	72.5	62.1	2.7
500 °C for 1 h)	Pt^{4+}	74.9	25.5	2.9

to 675 °C) are shown in Figure 12a–f. The binding energy of Ti(2p_{3/2,1/2}) at 459.0 and 464.8 eV in TiO₂ corresponds to Ti in the 4+ state (Figure 12a). Ti(2p_{3/2,1/2}) peaks are observed at 459.0 and 464.8 eV showing Ti in the 4+ state in Ce_{0.6}Ti_{0.4}O₂ (Figure 12b). The Ti⁴⁺ ion in Ce_{1-x}Ti_xO₂, upon hydrogen reduction in the TPR up to 675 °C, is fully reduced to the 3+ state as can be seen from the peaks at 458.2 and 464.0 eV (Figure 12c).³¹ The Ti(2p_{3/2,1/2}) peaks in as-prepared 1 and 2 atom % Pt/Ce_{0.85}Ti_{0.15}O₂ are observed at 458.8 and 464.7 eV (Figure 12d,e) and Ti is essentially in the 4+ state. In the TPR reduced 2 atom % Pt/Ce_{0.85}Ti_{0.15}O₂ sample, Ti(2p_{3/2,1/2}) peaks are observed at 458.2 and 464.0 eV (Figure 12d,e) and Ti is shows that all the Ti⁴⁺ are reduced to the 3+ state.



Figure 11. XPS of the Pt(4f) core level in (a) $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$, (b) $Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2-\delta}$, (c) $Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2-\delta}$ (reduced up to 675 °C in H₂), and (d) $Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2-\delta}$ (reoxidized in air at 500 °C).



Figure 12. XPS of the Ti(2p) core level from (a) TiO₂, (b) $Ce_{0.6}Ti_{0.4}O_2$, (c) $Ce_{0.6}Ti_{0.4}O_2$ (reduced up to 675 °C), (d) $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$, (e) $Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2-\delta}$, and (f) $Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2-\delta}$ (reduced up to 675 °C).



Figure 13. XPS of the Ce(3d) core level of (a) Ce_{0.6}Ti_{0.4}O₂, (b) Ce_{0.6}Ti_{0.4}O₂ (reduced in H₂ up to 675 °C), (c) Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2- $\delta}$} (reduced up to 675 °C), and (d) Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2- δ} (reoxidized in air at 500 °C).

The Ce(3d) core level regions of Ce_{0.6}Ti_{0.4}O₂, Ce_{0.6}Ti_{0.4}O_{1.73} (H₂ reduced up to 675 °C), 2 atom % Pt/Ce_{0.85}Ti_{0.15}O₂ (reduced in H₂ up to 675 °C), and the same sample air oxidized at 500 °C are given in Figure 13, curves a–d, respectively. Ce is present in the 4+ state in Ce_{1-x}Ti_xO₂. The Ce(3d) spectrum is similar to that of CeO₂ with 3d_{5/2} peaks at 882.9 and 901.3 eV and the corresponding satellites are at 889 and 899 eV for 3d_{5/2}.³² After TPR up to 675 °C, Ce in the 3+ as well as the 4+ states are observed as can be seen from the satellites due to the 3+ state (marked with an asterisk) and the 4+ state (marked with



Figure 14. Valence band spectra of (a) pure CeO₂, (b) Ce_{0.6}Ti_{0.4}O₂ (reduced up to 675 °C), (c) Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2- δ}, (d) Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2- δ} (reduced up to 675 °C), (e) PtO₂, and (f) Pt metal.

a plus sign). However, TPR reduced Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2– δ} show Ce mostly in the 4+ state (compare curves a and c in Figure 13c). The same sample upon air oxidation shows Ce in the 4+ state. Significant reduction of Ce⁴⁺ to Ce³⁺ in the TPR reduced Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2– δ} is not observed. The TPR reduced sample was black, but upon exposure to air while transferring to the XPS chamber the sample turned gray and, therefore, the Ce ion seems to become oxidized even at room temperature to the 4+ state.

In Figure 14, valence band spectra of CeO₂, Ce_{0.6}Ti_{0.4}O₂ reduced up to 675 °C, Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2- δ}, and the H₂-reduced

Ce_{0.83}Ti_{0.15}Pt_{0.02}O_{2- δ} are given. VB of Pt metal and PtO₂ are also given in the figure. In CeO₂, the valence band consists of O(2p) peaked at 6.5 eV and no electron density up to ~3 eV from E_F . Pure TiO₂ also shows a similar valence band due to O(2p).³³ On hydrogen reduction, the Ti³⁺ state with the Ti-(3d¹) band with measurable electron density below E_F and above the O(2p) band edge is observed as can be seen by curve B in Figure 14. In the Pt ion substituted sample and the reduced sample (curves C and D in Figure 14) also, an increase in the electron density below E_F is visible. Very high electron density at E_F is seen in Pt metal and the valence band extends up to 6 eV. PtO₂ also shows high electron density just below E_F due to the Pt(5d) band. Since the extent of Ce⁴⁺ reduction is small, the Ce(4f¹) peak at ~2 eV is not discernible in the VB region.

Discussion

Our interest in this study was to see how Ti⁴⁺ ionic substitution for Ce⁴⁺ in CeO₂ influences redox properties of CeO_2 and $Ce_{1-x}Pt_xO_{2-\delta}$. In our earlier studies, we had shown that $-Ce^{4+}-O-Pt^{2+}-\Box-Ce^{4+}$ interaction in $Ce_{1-x}Pt_xO_{2-\delta}$ is responsible for dissociated hydrogen adsorption at low temperature. Further, CO adsorption over Pt²⁺ sites and higher dissociative chemisorption of oxygen over oxide ion vacancy sites around Pt²⁺ leading to higher CO oxidation activity were shown. Here, formation of $Ce_{1-x}Ti_xO_2$ (x = 0.1-0.4) solid solution by the combustion method is confirmed from XRD studies. Pure CeO₂ is reduced to CeO_{1.96} in H₂ up to 675 °C and TiO₂ to TiO_{1.92}. However, $Ce_{1-x}Ti_xO_2$ can be reduced to a greater extent. That Ti^{4+} in $Ce_{1-x}Ti_xO_2$ is reduced to the Ti^{3+} state fully is shown by XPS. With 15% Ti⁴⁺ ion substitution, Ce_{0.85}Ti_{0.15}O₂ could be reduced to Ce_{0.85}Ti_{0.15}O_{1.86}. This means 15% of Ti^{4+} is reduced to the Ti^{3+} state and 15% of Ce^{4+} can be reduced to the Ce3+ state compared with just 8% in pure CeO_2 and 16% of Ti⁴⁺ in TiO₂. $Ce_{0.6}Ti_{0.4}O_2$ could be reduced to Ce_{0.71}⁴⁺Ce_{0.14}³⁺Ti_{0.4}³⁺O_{1.73} retaining the gross fluorite structure that can be oxidized back to Ce_{0.6}Ti_{0.4}O₂. Thus, reducibility of $Ce_{1-x}Ti_xO_2$ is higher than that of CeO_2 or TiO_2 .

The Ti⁴⁺ ion is too small to occupy the 8-coordinated Ce⁴⁺ site in the CeO₂ structure. The Ce–O bond length is 2.34 Å. With the lattice parameter of 5.372 Å for Ce_{0.6}Ti_{0.4}O₂, Ce–O and Ti-O bond lengths should be 2.32 Å. The Ti⁴⁺ ion with size 0.74 Å, being much smaller than Ce⁴⁺ (0.98 Å), prefers 6 coordination as in anatase or rutile phases. Ti-O bond distances are 1.96 and 1.93 Å in the TiO₂ anatase phase. The Ce_{1-x}Ti_xO₂ phase shows large line broadening in the XRD (see Figure 7) suggesting that oxide ion sublattice may be distorted leading to a change in the local coordination around the Ti⁴⁺ ion. It is possible that local coordination of Ti can be 6+2. This means $6\ O^{2-}$ of the 8 oxide ions come closer from the mean of 2.32 Å to ~ 2 Å due to the smaller Ti⁴⁺ ion and the remaining two oxide ions may move to longer distances. The oxide ions moving away from the shorter Ti-O distances must be easier to remove by H₂ thus explaining the higher reduciablity of $Ce_{1-x}Ti_xO_2$. Since oxide ion is bonded to both Ti⁴⁺ and Ce⁴⁺ ions, both of them are reduced. In $Ce_{1-x}Cu_xO_{2-\delta}$, for example, the extent of Ce4+ ion reduction was higher due to Cu2+ ion substitution.20 In Ce_{1-x}Zr_xO₂, 4+4 coordination for the Zr^{4+} ion is suggested to explain the high reducibility of the Ce⁴⁺ ion due to the Zr⁴⁺ ionic substitution.³⁴ A detailed local structure of the Ti⁴⁺ ion in CeO₂ by EXAFS is essential to understand higher chemical reactivity. A more interesting point is its reducibility in the Pt ion substituted Ce0.85Ti0.15O2. XRD, TEM, and XPS studies indicated clearly that Pt is in the ionic state. Since Pt is present mainly in the 2+ state, oxide ion vacancies need to be created. Therefore, we can write the formula of the compound as $Ce_{0.85-x}Pt_xTi_{0.15}O_{2-\delta}$. The exact composition of oxide ions is difficult to ascertain. However, this compound can be reduced to a greater extent than $Ce_{0.85}Ti_{0.15}O_2$. While $Ce_{0.85}Ti_{0.15}O_2$ can be reduced to $Ce_{0.70}^{4+}Ce_{0.15}^{3+}Ti_{0.15}^{-3+}O_{1.86}$, $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$ can be reduced to $Ce_{0.52}^{+4}Ce_{0.32}^{+3}Ti_{0.15}^{-3+}Pt_{0.01}^{-0+2}O_{1.75}$ up to 675 °C. This means, more Ce^{4+} can be reduced with Pt^{2+} ionic substitution in $Ce_{1-x}Ti_xO_2$.

The Ce(4f) band lies about 2 eV below the $E_{\rm F}$ as observed from the valence band spectrum of Ce_2O_3 .³² In CeO_2 it is empty. Pt metal has a high electron density at $E_{\rm F}$ (Figure 14). Even in PtO_2 where Pt is in the 4+ state, Pt(5d) electrons have sufficiently high electron density at $E_{\rm F}$. Certainly, Pt in the 2+ state should have electron density sufficiently high near $E_{\rm F}$. In TiO_2 , the Ti(3d) band lying below the E_F is empty. The distinct Ti³⁺(3d) band peak at ~1.5 eV below $E_{\rm F}$ is well separated from the O(2p) band in Ti₂O₃.³³ Thus, Ti(3d), Pt(5d), and Ce(4f) bands overlap below $E_{\rm F}$ and, therefore, any change in the electron density due to reduction of Pt²⁺ ion to Pt^o should populate Ti(3d) and Ce(4f) levels. Since the Pt° (6s²+5d⁸) band has high electron density at $E_{\rm F}$ and the Ti(3d) band lying below is empty in the Ti⁴⁺ state, oxidation of Pt^o to Pt²⁺ should occur, simultaneously reducing Ti4+ to the Ti3+ state. Increased reduction of Ti⁴⁺ and Ce⁴⁺ ion in the Pt-substituted sample is to be attributed to such an electronic interaction. Increase of CO oxidation rate over $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$ compared to $Ce_{0.99}Pt_{0.01}O_{2-\delta}$ should then be due to facile electron/hole transfer from Pt to Ti and Ce sites. Accordingly, the CO oxidation reaction can be written as follows:

$$O_{2} + 2V_{O_{2}^{-}}^{\bullet} \rightarrow 2O_{o}^{x} + 4h^{\bullet}$$

$$2[Ce^{4+}-O-Pt^{2+}-[O_{o}^{x}]-Ti^{4+}] + 2CO_{ads} \rightarrow$$

$$2CO_{2} + 2[Ce^{4+}-O-Pt^{o}-\Box-Ti^{4+}] + 2V_{O_{2}^{-}}^{\bullet}$$

$$2[Ce^{4+}-O-Pt^{o}-\Box-Ti^{4+}] + 2h^{\bullet} \rightarrow 2[Ce^{3+}-O-Pt^{2+}-\Box-Ti^{3+}]$$

$$2[Ce^{3+}-O-Pt^{2+}-\Box-Ti^{3+}] + 2h^{\bullet} \rightarrow [Ce^{4+}-O-Pt^{2+}-\Box-Ti^{4+}]$$

$$2CO + O_{2} = 2CO_{2}$$

From our XPS and hydrogen reduction studies, the reaction

$$O-Pt^{\circ}-\Box-Ti^{4+}-O+h^{\bullet} \rightarrow O-Pt^{2+}-\Box-Ti^{3+}-O$$

is more facile than Ce^{4+} -O-Pt^o- \Box - + $h^{\bullet} \rightarrow Ce^{4+}$ -O-Pt²⁺- \Box -. This should be expected because the Ti(3d) band is closer to the Pt(5d) band and electron or hole transfer from Pt(5d) to Ti(3d) is more facile. Thus, the reason for higher catalytic activity for CO oxidation is due to energetically more favorable electron transfer from Pt(5d) to Ti(3d) than Pt(5d) to Ce(4f). If such a proposition is correct, Ti_{1-x}Pt_xO_{2- δ} should be much more active for CO oxidation than the Pt-substituted Ce_{1-x}Ti_xO₂. Indeed, Ti_{0.99}Pt_{0.01}O_{2- δ} was prepared by the solution combustion method and the formation of Ti_{0.99}Pt_{0.01}O_{2- δ} in the anatase phase with Pt in the 2+ and the 4+ states has been well characterized.³⁵ The CO oxidation over Ti_{0.99}Pt_{0.01}O_{2- δ} under the same experimental condition as in Figure 1 indeed shows T₅₀ at 140 °C (see Figure 1). This confirms that the Pt(5d) \rightarrow Ti(3d) interaction is responsible for the enhanced catalytic behavior.

While TiO₂ (anatase) itself is a good reducible support, the oxide transforms to TiO₂ (rutile) above 650 °C³⁶ whereas $Ce_{1-x}Ti_xO_2$ is stable up to 750 °C without any TiO₂ separation. Pt ion substitution in $Ce_{1-x}Ti_xO_2$ has been possible and the

compound is stabe up to 750 °C. Further, restoration of metals in the oxidized state, viz., Pt²⁺, Ti⁴⁺, and Ce⁴⁺, as in the above reaction scheme is essential for high TOF. The Ce³⁺ ion is more easily oxidizable than Ti³⁺ to Ti⁴⁺. Therefore, from the catalysis consideration, Ce_{1-x}Ti_xO₂ as a support is more important than pure TiO₂.

Conclusions

(a) $Ce_{1-x}Ti_xO_2$ (x = 0.1-0.4) solid solutions were synthesized by the solution combustion method.

(b) $Ce_{1-x-y}Ti_xPt_yO_2$ (x = 0.15; y = 0.01-0.02) crystallites synthesized by a single step synthesis show that Pt is mainly in the Pt²⁺ state.

(c) H/Pt molar ratios are 5 and 4 over $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_2$ and $Ce_{0.99}Pt_{0.01}O_{2-\delta}$, respectively, and the ratio is just 0.078 over about 8 nm Pt metal particles at 30 °C.

(d) Reducibility of $\overline{CeO_2}$ is enhanced by Ti^{4+} ion substitution in $Ce_{1-x}Ti_xO_2$ (x = 0.0-0.4), and Pt ion substitution in $Ce_{1-x}Ti_xO_2$ enhances its reducibility further compared to that of the Pt ion in CeO₂.

(e) The rate of CO conversion over $Ce_{0.84}Ti_{0.15}Pt_{0.01}O_{2-\delta}$ is 45 times higher than that over $Ce_{0.99}Pt_{0.01}O_{2-\delta}$ at 155 °C.

(f) Electronic interaction between Ce⁴⁺–Ce³⁺, Ti⁴⁺–Ti³⁺, and Pt²⁺–Pt° via overlap of Ce(4f), Pt(5d), and Ti(3d) states in the valence band of Ce_{1-x-y}Ti_xPt_yO_{2- δ} is suggested to be responsible for faster electron transfer for higher CO + O₂ catalytic activity.

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Supporting Information Available: Hydrogen uptake as a function of time at 30 °C over $Ce_{0.83}Ti_{0.15}Pt_{0.02}O_2$ is given in Figure S1, the Rietveld refined XRD profile of $Ce_{0.9}Ti_{0.1}O_2$ in Figure S2, and the Rietveld refined XRD profile for 1% and 2% Pt in $Ce_{0.85}Ti_{0.15}O_2$ in Figure S3a and S3b, respectively. This material is available free of charge via the Internet at http://pubs.acs.org.

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