Influence of cerium precursor on the size and solid solubility of transition metals in combustion synthesized Ce$_{1-x}$M$_x$O$_2$\textsubscript{8} (M = Cu, Pd) nano crystallites: Enhancement of redox properties and catalytic activity

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Two cerium precursors have been employed to synthesize Ce$_{1-x}$M$_x$O$_2$\textsubscript{8} (M = Cu, Pd) nano-crystalline catalysts by solution combustion method. These nano materials have been characterized by X-ray diffraction (XRD), X-ray photoelectron spectroscopy (XPS), transmission electron microscopy (TEM) and BET surface area measurement. Redox behaviour of the catalysts was investigated by temperature-programmed reduction (H$_2$ TPR). Use of ceric ammonium nitrate (precursor A) gives ceria crystallites of size 30-45 nm while cerious nitrate (precursor B) gives 10-15 nm sized crystallites indicating three fold decrease in crystallite size of CeO$_2$. Solid solubility of copper in CeO$_2$ matrix is between 5-10 atom % with precursor A and it increases to 10-15 atom % with precursor B. The crystallite size is between 15-20 nm using B precursor compared to 40-50 nm crystallites with precursor A when Pd was substituted for Ce indicating approximately a two-fold decrease. With precursor A, solid solubility of Pd in ceria is between 3-5 atom % which increases to ~10 atom % with precursor B. Structural study shows M$^{2+}$ ion substitution into CeO$_2$ matrix. The enhancement of solid solubility coupled with the decrease in crystallite size is associated with an increase in oxygen storage capacity and catalytic activity for CO oxidation by O$_2$ and NO reduction by CO. Such an approach to synthesis of transition metal ion substituted nano CeO$_2$ is leading to catalysts with higher catalytic activity.

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Much research interest has been directed during the last few decades for the development of suitable catalysts for the removal of pollutants from various sources. Carbon monoxide and hydrocarbon oxidation reactions as well as nitric oxide reduction by CO over Group VIII metals have been extensively studied due to their practical importance in the control of emissions. Noble metals (Pt, Pd, Rh) supported on oxides, primarily Al$_2$O$_3$, are generally employed for this purpose where CeO$_2$ is added as the promoter because of its several beneficial effects\textsuperscript{1,2}. Among the transition metals, copper supported oxides are well studied, CO and methane oxidation and NO reduction over Cu--Ce--O system have been demonstrated by a number of groups\textsuperscript{3-7}. Highly dispersed CuO over CeO$_2$ support was believed to be the active phase, and a synergistic reaction pathway involving simultaneous reduction or oxidation of CeO$_2$ and copper oxides with CO or O$_2$, respectively, has been proposed to explain the enhanced catalytic activity in CO oxidation\textsuperscript{8-11}. Wrobel et al.\textsuperscript{12} have proposed a mechanism of hydrogen storage in CeM$_x$ mixed oxides based on the formation of anion vacancies due to insertion of M$^{2+}$ ion. The enhancement of redox property in Y--Ce--Zr--O mixed oxides on copper incorporation has been reported by Kulyova et al.\textsuperscript{13}. Like other noble metals, the catalytic activity of Pd supported catalysts has been studied for NO reduction, CO, and hydrocarbon oxidation reactions\textsuperscript{14-19}. Fernández-García et al.\textsuperscript{20,21} have studied the influence of ceria on the redox behaviour of alumina-supported copper catalysts and catalytic activity of Pd for CO oxidation by O$_2$.

The factors that influence the catalytic activity of the dispersed metals on the oxide support are: size, shape, extent of dispersion, relative amount of metals present, chemical nature of the support and the strength of interaction between the support and the metal\textsuperscript{22}. In most of these studies, the exact nature of the active site and the exact role of CeO$_2$ in terms of M--CeO$_2$ interaction is less understood. Bernal et al.\textsuperscript{23} have recently reviewed some aspects on metal/support interaction effects in NM/CeO$_2$ (NM: noble metal) catalysts. Activity of an oxide catalyst can be higher.
in a crystalline state compared to the same in an amorphous state because of the well-defined structure of the former. High surface area materials need not be crystalline but nano-crystalline materials will have high surface area. Method of preparation plays an important role on the behaviour of these catalysts. Conventionally, the metals are dispersed over the oxide support by co-precipitation, deposition, impregnation, ion-exchange, sol-gel, or incipient wetness methods. Patil et al. introduced the combustion method, which involved the combustion of the metal nitrates with different fuels and also the combustion of redox compounds for the preparation of nano-crystalline ceria, zirconia, and ceria-zirconia mixed oxides. Nano-crystalline CeO$_2$ has also been prepared by the homogeneous precipitation method, hydrothermal method, flux method, thermal hydrolysis method, and the semi-batch reactor method. The CuO/CeO$_2$ catalyst materials are conventionally prepared by co-precipitation and impregnation methods. Tschöpe et al. have reported the synthesis and redox activity of nano-crystalline Cu–CeO$_2$ catalysts with high CO oxidation activity by an inert gas condensation method, whereas Skárman et al. have studied the morphology and structure of CuO/CeO$_2$ nanocomposites prepared by the same method over the entire range of 2-98 atom % Cu. Zhang et al. studied the enhancement of oxygen storage capacity of nanophase solid solutions of Ce$_{0.9}$M$_{0.1}$O$_2$ prepared through co-precipitation method. The copper-ceria catalytic systems have also been reported to be active for H$_2$O decomposition, wet oxidation of phenol, selective oxidation of CO, low temperature water gas shift reaction and steam reforming of methanol. Wang et al. have shown the superiority of a surfactant-assisted synthesis method over precipitation method for the preparation of Pd/ceria catalyst.

In recent years, we have reported the synthesis of ceria supported transition metal catalysts by solution combustion method, which are found to have high three-way catalytic (TWC) activity, namely, CO oxidation, NO reduction by CO, and hydrocarbon oxidation. I onically dispersed metal ions on the CeO$_2$ surface leading to the formation of Ce$_{1-x}$M$_x$O$_{2.5}$ solid solution (where M = Cu, Pd, Pt) have been shown to be the determining factor for such high catalytic activity. The sizes of the crystallites obtained were in the range of 30-45 nm. A recent study by Shan et al. is another support to the idea of solid solution formation, where nano-sized Ce$_{1-x}$Cu$_x$O$_2$ (x≤0.1) materials prepared through complexation-combustion method have been found to improve the redox property. Now, the question is: what is the limiting size of the crystallites that can be achieved by employing solution combustion method and whether it is possible to substitute more transition metals as ions by decreasing the size of the CeO$_2$ crystallites.

Keeping this in mind, we proceeded to search for different cerium precursors and found cerrous nitrate, the use of which drastically reduces the size of the crystallites and enhances dispersion of the transition metal ion. In this paper, we show that by decreasing the crystallite size of CeO$_2$, more of Cu and Pd ions can be substituted which in turn show enhanced catalytic activity for CO oxidation and NO reduction.

Materials and Methods

Catalyst preparation—The combustion using cerrous nitrate as cerium precursor was carried out in an open furnace kept in a fume cupboard with exhaust. Oxalyldihydra zide (ODH, C$_2$H$_6$N$_4$O$_2$) prepared from diethyl oxalate and hydrazine hydrate was used as the fuel. The combustion mixture for the preparation of 5% Cu/CeO$_2$ contained Ce(NO$_3$)$_3$.6H$_2$O (Rolex Chemical Industries, 99.9%), Cu(NO$_3$)$_2$.3H$_2$O (S. D. Fine-Chem Ltd., 99.9%) and ODH in the mole ratio 0.95:0.05:1.475. For the preparation of 2% Pd/CeO$_2$, Ce(NO$_3$)$_3$.6H$_2$O, PdCl$_2$ (S. D. Fine-Chem. Ltd., 99.9%) and ODH were taken in the mole ratio 0.98:0.02:1.47.

In a typical preparation, 10 g of Ce(NO$_3$)$_3$.6H$_2$O, 0.293 g of Cu(NO$_3$)$_2$.3H$_2$O and 4.227 g of ODH were dissolved in 50 mL of distilled water in a beaker of 2 L capacity. The excess water was then evaporated and the redox mixture was placed on an open furnace maintained at ~350°C and covered with a lid keeping a little opening for the escape of liberated gases. Initially, the solution boils with frothing and foaming followed by complete dehydration when the surface gets ignited, and burns with a flame (~1000°C) yielding a voluminous solid product within 5 min. The product, deposited over the inner walls and the lid, was transferred into a boro silicate dish, covered with a watch glass, and introduced into a muffle furnace at 500°C for about 30 min to remove any residual volatile matter. Similarly, pure CeO$_2$, 1-4%, 10%, 15% Cu/CeO$_2$ catalysts, and 1-3%, 5%, 10%...
Pd/CeO₂ catalysts were prepared by this method. Preparation of CeO₂, Cu/CeO₂, and Pd/CeO₂ using ceric ammonium nitrate (precursor A) is described elsewhere. CuO was prepared by the combustion of copper nitrate with ODH. From now onwards, catalysts obtained from ceric ammonium nitrate precursor will be denoted as A catalyst and that from cerrous nitrate will be named as B catalyst.

** Catalyst characterization — XRD data of all the catalysts were recorded on a Philips X’Pert diffractometer at a scan rate of 0.5° min⁻¹ with 0.02° step size in the 2θ range 20-80°. The structural refinement was done using the FullProf-fp2k program. TEM studies were carried out using a JEOL JEM-200CX transmission electron microscope operated at 200 kV. BET surface area of the samples was determined by nitrogen adsorption-desorption method at liquid nitrogen temperature using a Quantachrome NOVA 1000 surface area analyzer. Prior to the analysis, the samples were degassed for 2 h at 200°C. XPS of the catalysts were recorded using an ESCA-3 Mark II spectrometer (VG Scientific Ltd., England) employing AlKα radiation (1486.6 eV) at an analyzer base pressure of 10⁻⁷ Torr. Binding energies were corrected for charge effects by reference to the C(1s) peak of carbon contamination at 285 eV and measured with a precision of ±0.2 eV. The experimental data were curve fitted with Gaussian peaks after subtracting a linear background.

** H₂ uptake measurement — Hydrogen uptake experiments were performed in a continuous flow gradientless quartz micro-reactor of length 30 cm and 0.4 cm internal diameter with 5.49% H₂/Ar flowing at 30 scm at a linear heating rate of 10°C min⁻¹. The flow temperature was achieved through cooling by liquid nitrogen flush for a few minutes. A thermal conducting detector (TCD), calibrated against pure CuO, was used to monitor the hydrogen concentration. The plot of TCD signal vs. temperature for a given system is recorded by continuously programming the temperature.

** Temperature-programmed reaction (TPR) — The catalytic testing was done in a temperature programmed reaction system equipped with a quadrupole mass spectrometer SX200 (European Spectrometry Services) for product analysis in a packed bed tubular quartz reactor (dimension 0.4 cm × 25 cm) at atmospheric pressure. Typically, 150 mg of the catalyst (40/80 mesh) diluted with/without SiO₂ (30/60 mesh size) was loaded in the reactor to get 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 scm using He as the balance to achieve a Gas Hourly Space Velocity (GHSV) of 43000 h⁻¹. The CO oxidation was carried out under excess oxygen with a feed gas composition of 2 vol % CO and 6 vol % O₂. The NO reduction by CO was performed under stoichiometric composition with 2 vol % NO and 2 vol % CO. The temperature was monitored by a fine chromel-alumel thermocouple inserted into the catalyst bed. Two mass flow sensors (Bronkhorst Hi-Tech BV and Honeywell AWM3100V) calibrated against standard bubble flow meter were used to monitor the gas flow.

Before the catalytic test, the as-prepared catalyst was heated at 200°C for 30 min followed by cooling in He flow (20 scm) to the experimental temperature to remove any adsorbed gas molecules. All the reactions were carried out as a function of temperature with a linear heating rate of 10°C min⁻¹. The gaseous products were sampled through a fine control leak valve to an ultra high vacuum (UHV) system housing the quadrupole mass spectrometer at 10⁻⁹ Torr. Final pressure of the gases in the vacuum system was 1x10⁻⁶ Torr. All the masses were scanned every 10 sec. At the end of the reaction, the intensity of each mass as a function of temperature (thermogram) was generated. Pure gases, CO, O₂, He, and mixed gases, 5.1% CO/He and 4.6% NO/He (certified calibration gas mixture) were obtained from Bhuruka Gases Ltd., Bangalore, having a purity better than 99.9%.

** Results  
** XRD studies — Figures 1a and 1b present the XRD patterns of CeO₂ and Cu/CeO₂ catalysts obtained from the two precursors employed respectively, in the 2θ range 25-55 degrees magnified by 20 times to check for the evolution of copper oxide phases with gradual increase in the Cu content in Cu/CeO₂ samples. All the diffraction lines could be indexed to the fluorite structure of ceria. The 5% Cu/CeO₂, A as well as B, did not show any trace of CuO in the XRD patterns. Peaks due to Cu₂O are also not detected. Small peaks at 20 values 35.5 and 38.7 degrees correspond to CuO in 10% Cu/CeO₂ (A). Thus, out of the 10 atom % copper taken in the preparation with precursor A, a small quantity of CuO gets separated. On the contrary, CuO peaks can barely be detected in 15 atom % Cu/CeO₂ (B). Thus, solid solubility of Cu²⁺...
Table 1 — Rietveld refined parameters of CeO$_2$ and Ce$_{1-x}$M$_x$O$_{2.5}$ crystallites

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>A (Å)</th>
<th>$R_{\text{Bragg}}$</th>
<th>$R_F$</th>
<th>$R_p$</th>
<th>occ$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$ (A)</td>
<td>5.4131 (6)</td>
<td>1.17</td>
<td>0.902</td>
<td>6.00</td>
<td>1.90 (3)</td>
</tr>
<tr>
<td>CeO$_2$ (B)</td>
<td>5.414 (1)</td>
<td>1.54</td>
<td>0.977</td>
<td>6.66</td>
<td>1.88 (3)</td>
</tr>
<tr>
<td>5% Cu/CeO$_2$ (A)</td>
<td>5.4127 (5)</td>
<td>1.15</td>
<td>0.874</td>
<td>5.62</td>
<td>1.85 (3)</td>
</tr>
<tr>
<td>10% Cu/CeO$_2$ (A)</td>
<td>5.4137 (5)</td>
<td>1.34</td>
<td>1.91</td>
<td>6.04</td>
<td>1.76 (3)</td>
</tr>
<tr>
<td>5% Cu/CeO$_2$ (B)</td>
<td>5.4135 (4)*</td>
<td>1.03*</td>
<td>0.756*</td>
<td>6.19*</td>
<td>1.80 (3)*</td>
</tr>
<tr>
<td>10% Cu/CeO$_2$ (B)</td>
<td>5.4117 (8)</td>
<td>1.39</td>
<td>1.12</td>
<td>6.71</td>
<td>1.84 (3)</td>
</tr>
<tr>
<td>15% Cu/CeO$_2$ (B)</td>
<td>5.414 (1)</td>
<td>1.71</td>
<td>1.41</td>
<td>6.90</td>
<td>1.77 (3)</td>
</tr>
<tr>
<td>5% Pd/CeO$_2$ (A)</td>
<td>5.4128 (6)</td>
<td>0.75</td>
<td>0.606</td>
<td>4.94</td>
<td>1.90 (2)</td>
</tr>
<tr>
<td>5% Pd/CeO$_2$ (B)</td>
<td>5.4115 (4)*</td>
<td>3.46*</td>
<td>1.93*</td>
<td>6.82*</td>
<td>1.87 (2)*</td>
</tr>
<tr>
<td>1% Pd/CeO$_2$ (A)</td>
<td>5.4120 (7)</td>
<td>1.40</td>
<td>1.12</td>
<td>6.35</td>
<td>1.89 (2)</td>
</tr>
<tr>
<td>5% Pd/CeO$_2$ (B)</td>
<td>5.4125 (6)</td>
<td>1.60</td>
<td>1.24</td>
<td>6.22</td>
<td>1.86 (2)</td>
</tr>
<tr>
<td>10% Pd/CeO$_2$ (B)</td>
<td>5.411 (1)</td>
<td>2.87</td>
<td>2.18</td>
<td>7.41</td>
<td>1.78 (2)</td>
</tr>
</tbody>
</table>

$^a$oxide ion occupancy; $^*$refined parameters from two-phase refinement

The ‘$a$’ value for the same is 5.4131 (6) Å. Pure CeO$_2$ (B) could be refined to $R_{\text{Bragg}}$ factor of 1.54%, with the cell parameter of 5.414 (1) Å. The oxygen deficiency in CeO$_2$ (A) is ~3.5% and that in CeO$_2$ (B) is ~4.5%. Thus, CeO$_2$ prepared by employing cerous nitrate gave nano particles of smaller size compared to that obtained with ceric ammonium nitrate precursor with higher oxide ion vacancy. Our findings are in agreement with the neutron diffraction study over ceria and ceria-zirconia carried out by Mamontov et al., where it was suggested that Frenkel type oxygen vacancies in the octahedral site are present along with the usual oxygen vacancies in tetrahedral sites of a fluorite lattice. The 10% Cu/CeO$_2$ (A) and 15% Cu/CeO$_2$ (B) samples were refined considering both, with CuO, and without CuO as the second phase. All the refined parameters, $R_{\text{Bragg}}, R_F,$ and $R_p,$ lattice parameter ‘$a$’, and oxygen occupancy have been listed in Table 1. The 10% Cu/CeO$_2$ (A) has been refined for Cu$_{0.06}$Cu$_{0.04}$O$_{0.8}$ with $R_{\text{Bragg}}, R_F,$ and $R_p$ values of 1.03, 0.756, 6.19%, respectively. The lattice parameter ‘$a$’ is 5.4135 (4) Å. The refined parameters, ‘$a$’, $R_{\text{Bragg}}, R_F,$ and oxygen occupancy for 15% Cu/CeO$_2$ (B) are respectively 5.4109 (9), 1.96, 1.15, 6.86, and 1.68 (3) with two-phase (with 2 atom % CuO) refinement, whereas the corresponding values are 5.412 (1), 2.93, 1.92, 7.16, and 1.64 (3), when single-phase refinement was carried out. The improved $R$ factors with two-phase refinement indicate the presence of a little CuO in 10 atom % Cu/CeO$_2$ (A), and 15 atom % Cu/CeO$_2$ (B).

ion in CeO$_2$ is between 5 and 10 atom % with precursor A, and between 10 and 15 atom % with precursor B. All the XRD patterns are Rietveld refined by simultaneously varying 19 parameters, which include overall scale factor, background parameters, unit cell, half width, shape, and isotropic thermal parameters along with the oxygen occupancy. The profile fitting (not shown) is good with pseudo-Voigt function and there seems to be no residual background indicating high crystallinity of the prepared samples. For CeO$_2$ (A), $R_{\text{Bragg}}$ is 1.17%, and
Fig. 2—XRD patterns of Pd/\(\text{CeO}_2\) catalysts from (a) Precursor A and (b) Precursor B in the 20 range 25–55°. [Each pattern is magnified 20 times with respect to the corresponding CeO\(_2\) (111) peak.]

Fig. 3—TEM images of (a) \(\text{CeO}_2\) (A), (b) \(\text{CeO}_2\) (B), (c) 5% Cu/\(\text{CeO}_2\) (A), (d) 5% Cu/\(\text{CeO}_2\) (B), and (e) 15% Cu/\(\text{CeO}_2\) (B), and (f) ED pattern of 15% Cu/\(\text{CeO}_2\) (B).
Figures 2a and 2b depict the XRD patterns of Pd/CeO₂ catalysts after 20 times magnification as was done for Cu/CeO₂ samples. All the catalysts crystallize in the fluorite structure (Fm3m). Little amount of Pd metal gets separated in 5% Pd/CeO₂ (A); whereas up to the detection limit of XRD, no signature of either Pd metal or Pdo is observed even in the XRD pattern of 10% Pd/CeO₂ (B). This indicates the enhancement of solid solubility of Pd in ceria matrix by at least two times when cerous nitrate is employed instead of ceric ammonium nitrate for the synthesis of Pd/CeO₂ catalyst. The 5% Pd/CeO₂ (A) XRD data has been Rietveld refined for Ce₀.₉₇Pd₀.₀₃O₁₈₁₈ with REmag=3.46%. The ‘a’ value for this catalyst is 5.4115 (4) Å. For 5% Pd/CeO₂ (B), the REmag, R₀ and Rₚ values are 1.60, 1.24, and 6.22%, respectively and the cell parameter is 5.4125 (6) Å. Similarly, the 10% Pd/CeO₂ (B) has been refined for REmag=2.87% with cell parameter a=5.411 (1) Å.

In general, the diffraction lines from the B precursor are much broader than that from the A precursor. Average crystallite size of the CeO₂ and Ce₁₅Cu₀₅O₂₆ catalysts from the A precursor are of the order of ~35 nm as calculated using the Scherrer formula and that of the B catalysts are ~15 nm. The average crystallite size is ~10 nm for the Ce₁₅Pd₀₅O₂₆ (A) catalyst and it is ~20 nm for the Ce₁₅Pd₀₅O₂₆ (B) catalysts.

TEM studies—Typical TEM images of CeO₂ and 5% Cu/CeO₂ catalysts from the two precursors along with that of 15% Cu/CeO₂ (B) are shown in Figs 3a-3e. The morphology of CeO₂ crystallites is cubic, edges of which are sharp. The size of the crystallites is in the range 30-45 nm for A sample, and 10-15 nm for B sample which agrees well with the XRD measurements. No notable change in the TEM image of 15 atom% Cu/CeO₂ is observed (Fig. 3e). Particle sizes are of the order of 15 nm. Copper oxide particles on the crystallite surfaces could not be detected. The ring type diffraction pattern could be indexed only to polycrystalline CeO₂ in fluorite structure, and diffraction rings or spots corresponding to any of the oxides of Cu haven’t been observed even in the ED pattern of 15 atom% Cu/CeO₂ (B) (Fig. 3f). The fact that Cu/CeO₂ crystallites are of smaller size in comparison to pure ceria may be due to the surface segregation of copper ions (as described later from XPS studies), hindering the growth of CeO₂ crystallites.

Representative TEM images with the corresponding ED pattern of Pd/CeO₂ catalysts are shown in Fig. 4. Here, we note that the 2 atom% Pd/CeO₂ (Fig. 4a) particles are of similar size as that of Cu/CeO₂ (A) samples, but the 5 atom% Pd/CeO₂ (Fig. 4c) particles are considerably larger, of the order of ~100 nm. No Pd metal is seen in the TEM image of the former catalyst, whereas 5-10 nm Pd metal particles are observed in the latter catalyst concordant with the XRD studies. This could be verified from the presence of Pd(111) diffraction ring in the latter (compare Figure 4d with 4b). Figure 4e presents the TEM image of 5% Pd/CeO₂ (B) catalyst for comparison. The cubic crystallites are in the range of 15-25 nm and no diffraction ring or spot other than that of ceria is found in the ED pattern of the same (Fig. 4f).

BET surface area—The surface areas of A and B catalysts are listed in Table 2. With the use of precursor B, we note approximately three-fold
Table 2 — Physical properties of \( \text{CeO}_2 \) and \( \text{Ce}_{1-x} \text{M}_{x} \text{O}_{2.5} \) catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Crystallite size (nm)</th>
<th>Surface area ( \text{m}^2 \text{ g}^{-1} )</th>
<th>( \frac{X_{\text{SM}}}{X_{\text{C}}} ) ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>( \text{CeO}_2 ) (A)</td>
<td>32</td>
<td>12 (26)</td>
<td>–</td>
</tr>
<tr>
<td>( \text{CeO}_2 ) (B)</td>
<td>14</td>
<td>40 (59)</td>
<td>–</td>
</tr>
<tr>
<td>5% Cu/( \text{CeO}_2 ) (A)</td>
<td>35</td>
<td>46 (24)</td>
<td>0.37</td>
</tr>
<tr>
<td>10% Cu/( \text{CeO}_2 ) (A)</td>
<td>37</td>
<td>20 (22)</td>
<td>0.46</td>
</tr>
<tr>
<td>5% Cu/( \text{CeO}_2 ) (B)</td>
<td>18</td>
<td>43 (46)</td>
<td>0.38</td>
</tr>
<tr>
<td>10% Cu/( \text{CeO}_2 ) (B)</td>
<td>15</td>
<td>52 (55)</td>
<td>0.44</td>
</tr>
<tr>
<td>15% Cu/( \text{CeO}_2 ) (B)</td>
<td>16</td>
<td>55 (52)</td>
<td>0.39</td>
</tr>
<tr>
<td>1% Pd/( \text{CeO}_2 ) (A)</td>
<td>41</td>
<td>20 (20)</td>
<td>0.038</td>
</tr>
<tr>
<td>2% Pd/( \text{CeO}_2 ) (A)</td>
<td>42</td>
<td>22 (20)</td>
<td>0.077</td>
</tr>
<tr>
<td>5% Pd/( \text{CeO}_2 ) (A)</td>
<td>43</td>
<td>21 (19)</td>
<td>0.120</td>
</tr>
<tr>
<td>1% Pd/( \text{CeO}_2 ) (B)</td>
<td>18</td>
<td>37 (46)</td>
<td>0.032</td>
</tr>
<tr>
<td>2% Pd/( \text{CeO}_2 ) (B)</td>
<td>22</td>
<td>42 (38)</td>
<td>0.068</td>
</tr>
<tr>
<td>5% Pd/( \text{CeO}_2 ) (B)</td>
<td>19</td>
<td>35 (44)</td>
<td>0.129</td>
</tr>
<tr>
<td>10% Pd/( \text{CeO}_2 ) (B)</td>
<td>18</td>
<td>38 (46)</td>
<td>0.236</td>
</tr>
</tbody>
</table>

* Determined from \( \text{CeO}_2 \) (111) reflection according to the Scherrer formula; \( \text{surface area obtained from the BET method; surface area calculated considering cubic crystallites of the size obtained from Scherrer formula; surface concentration of copper or palladium obtained from XPS.}

increase in the surface area for \( \text{Ce}_{1-x} \text{Cu}_{x} \text{O}_{2.5} \) catalysts whereas it is increased by two times for the \( \text{Ce}_{1-x} \text{Pd}_{x} \text{O}_{2.5} \) catalysts. This is in conformity with the decrease in the crystallite size in the B catalysts as observed from the XRD and TEM studies.

**XPS studies** — Figure 5 shows the Cu(2p) core level region of the 5% Cu/\( \text{CeO}_2 \) catalysts along with that of the parent oxide, CuO, for comparison. Accordingly, the Cu(2p/2, 3/2) peaks at 933.8 and 953.8 eV with satellites centered at 9 eV below the main peak in 5 atom % Cu/\( \text{CeO}_2 \) clearly can be attributed to Cu in +2 oxidation state. The satellite to main Cu peak (Cu2p3/2) ratio \( (S/M) \) of 5 atom % copper substituted ceria is 0.58 and 0.57, respectively for A and B catalysts. The ratios vary between 0.57 and 0.60 depending on the copper substitution. The \( S/M \) value for CuO is 0.62 and it varies from 0.37 to 0.47 for Cu2+ ion in square pyramidal position in \( \text{Bi}_2 \text{Cu}_1 \text{R}_1 \text{Sr}_2 \text{Cu}_2 \text{O}_{5.5} \) \( \text{R} = \text{Y, Yb} \). Further, the \( S/M \) values are 0.55 and 0.85 for Cu2+ in octahedral and tetrahedral sites of a cubic spinel, respectively. Thus, Cu2+ ion in \( \text{Ce}_{1-x} \text{Cu}_{x} \text{O}_{2.5} \) catalysts is not in tetrahedral coordination. The lower value of \( S/M \) does not support the presence of copper as CuO phase. The Cu(2p) core level region in 10% Cu/\( \text{CeO}_2 \) (A), 10% and 15% Cu/\( \text{CeO}_2 \) (B) has also been investigated.

Copper is found to be present in the +2 oxidation state in all the compounds with \( S/M \) ratio between 0.58 and 0.60. Figure 6 shows the Pd(3d) core level region of 2% Pd/\( \text{CeO}_2 \) (A and B), 5% Pd/\( \text{CeO}_2 \) (A and B) and 10% Pd/\( \text{CeO}_2 \) (B) catalysts. Accordingly, the Pd(3d3/2, 5/2)
The XPS of Ce(3d) region in CeO₂ (A), CeO₂-Pd (B), Cu/ CeO₂-Pd (C), 5% Cu/ CeO₂-Pd (D), 2% Pd/ CeO₂-Pd (E), 2% Pd/ CeO₂-Pd (F) are shown in the figure. Satellites for Pd(3d) peaks are observed at 335.2, 340.4, 341.7 eV. For PdCl₂, the Pd(3d) doublet (not shown in the figure) was observed at 338 and 343.3 eV. Thus, there is a shift of the 3d₅/₂ binding energy by 1.1-1.6 eV in Pd/ CeO₂ compared to that in PdO. This is significant and readily confirms that Pd in ceria matrix is different from that in PdO. The binding energy of Pd(3d) in Pd/ CeO₂ is close to that of PdCl₂, indicating the presence of palladium in highly ionic state in the ceria matrix. The Pd(3d) region in 5% Pd/ CeO₂ (A) and 10% Pd/ CeO₂ (B) can be deconvoluted into two pairs of spin-orbit doublets. The lower binding energy component in 5% Pd/ CeO₂ (A), which is found to be very small, is due to the Pd metal, the higher being due to Pd²⁺. No Pd metal component is seen in the XPS of 10% Pd/ CeO₂ (B). The lower intensity peaks at binding energies 335.9 and 341.0 eV are close to Pd²⁺ in PdO.

The XPS of Ce(3d) region in CeO₂, 5% Cu/ CeO₂ and 2% Pd/ CeO₂ catalysts obtained from both the precursors are plotted in Fig. 7. The Ce(3d₅/₂, 3/₂) peaks at -982.9 and -901.3 eV with satellite features (marked in the figure) correspond to CeO₂ with Ce in +4 oxidation state. The surface concentration of copper or palladium in the catalyst samples have been calculated employing the following relation:

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X_M = \frac{I_M \sigma_M \lambda_M D_E(M)}{X_C} \frac{I_C \sigma_C \lambda_C D_E(Ce)}{X_M I_C \sigma_C \lambda_C D_E(Ce)} \cdot \frac{X_C}{X_M} = X_{cu} X_{ce} \cdot X_{ce} = 0.37 \text{ for 5 atom % Cu/ CeO₂ (A) and that of the B catalyst is 0.38. Thus, out of 5 atom % Cu taken in the preparation the surface concentration of the same is 37% and 38%, respectively for the A and B catalyst. For 10 atom % copper substituted catalyst, the } X_{cu}/X_{ce} \text{ is about 0.45. The surface concentration of Pd (X_Pd/X_Ce) increases from 0.038 in 1 atom % Pd/ CeO₂ (A) to 0.12 in 5 atom % Pd/ CeO₂ (A). No significant change in surface concentration is noted in the B catalysts. Roughly, Pd surface concentration is four times the bulk concentration up to 2 atom % Pd/ CeO₂. Further increase of Pd content adversely affected the surface Pd concentration. Therefore, there is 4-7 times enhancement in surface concentration of Cu in Ce₁₋ₓCuₓO₂₋₃ catalysts, whereas Pd concentration is only 3-4 times that of bulk concentration for the Ce₁₋ₓPdₓO₂₋₃ catalysts, clearly indicating surface segregation of metal ions on CeO₂ crystallites surface. Hence, XPS study has confirmed ionic dispersion of M on the surface of CeO₂ crystallites. It will be shown later that 5 atom % Cu and 2 atom % Pd is sufficient to observe maximum catalytic activity which can be concluded from the XPS analysis since at these substitution levels, the surface concentration of metal ion is maximum.
Hydrogen uptake studies—Figure 8a shows the temperature programmed reduction (TPR) profiles for CuO, pure CeO₂, and Ce₁₋ₓCuₓO₂₋₈ catalysts. Pure CeO₂ (A as well as B) shows H₂ uptake (oxygen storage capacity) above 200°C and it consists of two peaks. The small first peak centred at ~435 and ~450 °C, respectively for A and B sample, can be traced to a global process corresponding to the consumption of surface oxygen species⁵⁷ and the redox process beyond 500°C is attributed to bulk reduction. The total volume of hydrogen consumed is 8.2 cm³ g⁻¹ up to 800°C for CeO₂ (A), which is equivalent to 4.1 cm³ of O₂ g⁻¹, corresponding to the reduction of CeO₂ to CeO₁.₉₄. The total hydrogen consumption over CeO₂ (B) is 9.9 cm³ g⁻¹, corresponding to the reduction of CeO₂ to CeO₁.₉₂. The hydrogen uptake during the first peak comes out to be 61 and 104 μmol g⁻¹, respectively for the A and B ceria. In a recent study, Perrichon et al.⁵⁸ have proposed a direct correlation between BET surface area and hydrogen uptake for CeO₂. From their studies, for CeO₂ (A) with a surface area of 12 m² g⁻¹, the H₂ uptake is 39 μmol g⁻¹ from the experimental curve and 55 μmol g⁻¹ from the symmetrical peak procedure. The expected value of H₂ uptake is 68 μmol g⁻¹ for this CeO₂ following the methodology of Johnson and Moo⁵⁹. For CeO₂ (B), these values are 136, 183, and 220 μmol g⁻¹, respectively. Our observed values of 61 and 104 μmol g⁻¹ are in close agreement with their studies. Peak reduction temperature of CuO is about 330°C. H₂ uptake over Cu/CeO₂ samples occurs between 100-250°C. The main peak centred at ~185°C for 1-4% Cu/CeO₂ (A), increases to 218°C for 5% Cu/CeO₂ (A) which further increases to 250°C for the 10% Cu/CeO₂ (A) catalyst. For the B catalysts, the main peak shifts from 212°C in 1% Cu/CeO₂ to 195°C in 10% Cu/CeO₂ and it is at 220°C for the 15% Cu/CeO₂ catalyst. In general, the reduction temperature is lower in the B catalyst than in the A catalyst, at least for the concentrations beyond 4 atom % copper substitution. The low temperature peak has been attributed to the reduction of Cu ions, which is followed by the reduction of CeO₂ at a higher temperature. That the Cu²⁺ ion in Ce₁₋ₓCuₓO₂₋₈ reduces to Cu⁺ after H₂ uptake has been
confirmed by the XPS study. Further, on passing oxygen at ~500°C after the H₂ uptake experiment, Cu⁺⁺ is oxidized back to Cu⁺⁺ as seen from the equivalent amount of hydrogen taken up. Thus, Cu⁺⁺ in Ce₄₋ₓCuₓOₓ₋₅ can be reduced or oxidized reversibly unlike pure CuO. Repeated oxidation-reduction cycles over the catalyst show very little decrease (~5%) in the extent of hydrogen uptake. Total amount of hydrogen taken up by copper has been estimated from the integrated area, and the H₂/Cu mole ratio is plotted in Fig. 8b as a function of the copper atomic percentage for both the A and the B catalysts. The H₂/Cu mole ratio is about 2.3 for A catalyst. However, the ratio is as high as 5 for 1 and 2 atom % Cu/CeO₂ (B) and decreases to 1.3 with the increase in Cu atom % to 15 atom % Cu/CeO₂ (B). The H₂/Cu ratio observed in the present study is higher than the reported value of 1.65 over Ce₀.₉₅Cu₀.₀₅O₂ by Shan et al. A drastic decrease in the reduction temperature of Cu²⁺ ions in CeO₂ at 215°C and lower compared to 330°C for pure CuO clearly demonstrates the absence of CuO phase. If Cu²⁺ ions were present in the form of CuO, H₂/Cu ratio should have been just 1 for the reaction CuO + H₂ → Cu + H₂O. The higher H₂/Cu ratio can only be explained by considering the reduction of part of Ce⁴⁺ ion (surface cerium ions) around the Cu²⁺ ions in Ce₁₋ₓCuₓO₂₋₅.

TPR profiles for PdO and Ceₓ₋₄PdₓO₂₋₅ catalysts are presented in Fig. 9a. The Ceₓ₋₄PdₓO₂₋₅ catalysts show H₂ uptake between 0 and 170°C. The TPR trace of bulk PdO shows the low temperature peak at 43°C with a negative peak at 74°C that has been attributed to the decomposition of Pd hydride. This negative peak is observed for 3 and 5 atom % Pd/CeO₂ (A) catalyst and is absent in all the other catalysts examined here. The reduction temperature decreases from 55°C in 1 atom % Pd/CeO₂ (A) to 25°C in 5 atom % Pd/CeO₂ (A). This is in agreement with the study of Jen et al., where the fresh 2 wt.% Pd/CeO₂ showed H₂ reduction peak at ~43°C. 1% Pd/CeO₂ (B) shows hydrogen uptake at 132°C, which decreases to 83°C when Pd substitution is increased to 5 atom %. There is a low temperature hydrogen consumption peak between 40-65°C over 2-5 atom % Pd/CeO₂ (B). Total amount of hydrogen taken up by palladium in ceria matrix has been estimated from the integrated area under the peak and the hydrogen to palladium mole ratio as a function of palladium loading is plotted in Fig. 9b for the both A and the B catalysts. The H₂/Pd mole ratio was found to decrease with increase of Pd loading. The ratio decreases from ~2 in 1% Pd/CeO₂ (A) to ~1 in 5% Pd/CeO₂. At least four moles of H₂ are taken per palladium by 1 atom % Pd/CeO₂ (B) which decreases to ~2.7 on increasing
Having characterized the transition metal ion substituted CeO$_2$ as giving Ce$_{1-x}$M$_x$O$_{2.5}$ and noting approximately 2 to 3 fold decrease in crystallite size respectively for Cu and Pd with high OSC, the B catalyst is predicted to show enhanced catalytic activity, at least two and three times more than the A catalyst. To understand this, CO oxidation by O$_2$ and NO reduction by CO were studied as probe reaction over these catalysts.

*Catalytic studies over CeO$_2$ and Cu/CeO$_2*—CO conversion efficiencies and the CO$_2$ formation rates of pure ceria (A and B) and different Cu substituted catalysts are compared in Fig. 10a. The B samples showed higher activity than the A samples at all temperatures. The CO oxidation is completed beyond 350°C over CeO$_2$ (B) compared to 415°C over CeO$_2$ (A), the light-off temperatures being 295°C and 307°C, respectively. Over 5% Cu/CeO$_2$ (A), the CO oxidation starts at 70°C and complete conversion occurs above 130°C. These temperatures are 60°C and 105°C, respectively for 5% Cu/CeO$_2$ (B). At 94°C, the CO conversion over 5% Cu/CeO$_2$ (B) is 50%, whereas it is mere 16% over 5% Cu/CeO$_2$ (A). Thus, at the light-off temperature, the activity of the B catalysts is nearly 3 times that of the A catalyst. The CO oxidation activity of 10 and 15% Cu/CeO$_2$ (B), and 10% Cu/CeO$_2$ (A) has also been tested. It shows no significant change in activity in comparison to the respective 5% Cu/CeO$_2$. The 5 atom % copper substitution is the optimum and hence NO+CO reaction was carried over these catalysts only.

Fig. 10b shows percent NO conversion as a function of temperature over 5 atom % Cu/CeO$_2$ catalysts. The figure also incorporates the conversion rate of NO. Since the mass numbers of CO$_2$ and N$_2$O are the same, an increase in CO$_2$/N$_2$O (m/z=44) concentration with a simultaneous decrease in NO (m/z=30) concentration was taken as a measure of NO conversion. Over 5 atom % Cu/CeO$_2$ (A), the NO reduction starts at 80°C and the reduction is completed beyond 330°C. These are respectively, 65°C, and 215°C over 5 atom % Cu/CeO$_2$ (B). The light-off temperature of the B catalyst is 117°C and that of the A catalyst is 190°C. At the light-off temperature of A catalyst, the NO reduction is already 95% complete over B catalyst.

*Catalytic studies over Pd/CeO$_2*—In Fig. 11a, we have compared the CO conversion efficiencies of different Pd substituted catalysts with varying Pd

Fig. 10 — (a) %CO conversion and CO$_2$ formation rate as a function of temperature over CeO$_2$ and Ce$_{1-x}$Cu$_x$O$_{2.5}$ catalysts from the two precursors employed, and (b) %NO conversion and NO conversion rate as a function of temperature over (a) 5% Cu/CeO$_2$ (A) and (b) 5% Cu/CeO$_2$ (B). Reaction conditions: CO= NO= 2 vol %, O$_2$= 6 vol %, He balance, Total Flow = 100 scmm, GHSV= 43 000 h$^{-1}$ and w = 150 mg.
substitution under identical experimental conditions.

The figure also includes the CO₂ formation rates. As seen from the figure, CO oxidation starts at 110°C over 1% Pd/CoO₂ (A) and it is complete at 230°C, the light-off temperature being 163°C. Catalytic activities of 2 and 3 atom % Pd/CoO₂ from A precursor are comparable, where an enhancement of activity in terms of lower reaction temperature and T₅₀ are noted. Over 5% Pd/CoO₂ (A), CO oxidation begins at 100°C and the complete CO conversion takes place at 195°C. In general, the activity of the A catalysts is maximum at 2% substitution level which decreases on increasing the Pd substitution to 5 atom %. In the B series, the CO oxidation activity increases from 1 atom % Pd/CoO₂ to 2 atom % Pd/CoO₂ and there occurs no significant enhancement in activity on increasing the Pd substitution level to 5 atom %. Over 1 atom % Pd/CoO₂ (B), CO oxidation starts at 120°C and is completed beyond 230°C. Both the temperatures are higher than that of 1 atom % Pd/CoO₂ (A). But in 2 atom % to 5 atom % Pd substituted ceria, the activity of B catalysts is much higher than that of the A catalysts at all temperatures. Over these catalysts, the oxidation begins at ~50°C and it is complete at 105±5°C. Whereas the CO oxidation is almost complete at 100°C over 2-5 atom % B catalyst, the conversion is merely 5% over 2-3 atom % A catalyst and it just starts over 5 atom % Pd/CoO₂ (A). Also, when the conversion reached 50% over 2-5 atom % Pd/CoO₂ (B) catalysts, no further reaction takes place over the A catalysts. Thus, the B catalysts are much more active than the A catalysts, 1 atom % Pd/CoO₂ (B) is an exception. Light-off temperature of 2-5 atom % Pd/CoO₂ (B) catalyst is lower than that of the 2-3 atom % Pd/CoO₂ (A) catalyst by ~40°. From the results obtained, it is evident that 2 atom % Pd substitution is optimum for all purposes and hence we carried out NO reduction by CO over only 2% Pd/CoO₂.

Figure 11b shows percent NO conversion as a function of temperature over 2 atom % Pd/CoO₂ catalysts along with the NO conversion rate. The NO reduction starts at 130°C over A catalyst and it is complete above 225°C. Over B catalyst, the reduction begins at 100°C and complete reduction is achieved beyond 190°C. The light-off temperature of the B catalyst (162°C) is lower by 32 degree than that of the A catalyst (194°C). At T₅₀ of the B catalyst the NO conversion is less, 9%, indicating enhancement of activity by the B catalyst by over five times. The NO conversion is 31% over A catalyst at 95% conversion temperature of the B catalyst. Thus, the smaller B crystallites show higher catalytic activity.

The catalytic oxidation of CO and the reduction of NO demonstrated 3-5 times higher catalytic activity over the smaller B crystallites compared to that of the larger A crystallites. The observed enhanced catalytic activity is much higher than that expected solely from the increase in surface area.

Discussion

The chemical reactions occurring in the combustion process with ceric ammonium nitrate and cerrous nitrate can be written as follows:
5(NH₄)₂Ce(NO₃)₆ + 12C₂H₆NiO₂ → 5CeO₂ + 44N₂ + 24CO₂ + 56H₂O \ldots (2)

4Ce(NO₃)₃ + 6C₂H₆NiO₂ + O₂ → 4CeO₂ + 18N₂ + 12CO₂ + 18H₂O \ldots (3)

In the case of cerrous nitrate, oxygen from the atmosphere is essential to convert Ce⁷⁺ to Ce⁴⁺. The most plausible reaction scheme with B precursor is: Ce(III)nitrate → Ce₂O₃ → CeO₂. The requirement of a finite time for this process does not allow the smaller CeO₂ crystallites to coagulate in comparison to those of the ceria crystallites formed by the combustion of Ce(IV) nitrate. This could be one of the reasons for the production of smaller CeO₂ particles.

It is to be noted that as the metal content is increased, a measurable decrease in the lattice parameter was observed. This is expected, since the ionic radius of Cu²⁺ (0.73 Å) and Pd²⁺ (0.86 Å) is smaller than that of Ce⁴⁺ (1.01 Å). However, a larger decrease in ‘a’ is expected. The simultaneous increase in oxide ion vacancy, which is indeed large, with the gradual incorporation of metal ions increases the lattice parameter. This may be the reason for not observing a much larger decrease in ‘a’. Also, the decrease in oxygen content is higher than that due to metal ion substitution for cerium ions. Since there is a large difference in the atomic numbers of cerium (58) and oxygen (8), scattering factors are largely different. Therefore, the exact value of oxygen occupancy cannot be ascertained but a systematic decrease in the oxygen content of the oxides with increase in metal content demonstrates lower valent metal ion substitution for Ce⁴⁺ ion. Decrease in the CeO₂ as well as Ce₁₋ₓCuₓO₂₋₀.5 crystallite size from 35 nm to 15 nm should show an increase in surface area by three times. Similarly, the surface area of Ce₁₋ₓPdₓO₂₋₀.5 catalysts is predicted to increase by two times. This is indeed observed experimentally (see Table 2). The surface areas were also calculated considering the cubic size of the crystallites as obtained from the Sherrer formula and they are listed in Table 2. In general, the measured BET areas are lower than the calculated ones, which indicate the dense nature of the crystallites.

The H₂ uptake measurement clearly demonstrated enhancement of redox property when copper/palladium is substituted for cerium in ceria, indicating definite metal-ceria interaction. The lowering of peak reduction temperature by ~140–80°C in Ce₁₋ₓCuₓO₂₋₀.5 catalysts from ~330°C in CuO indicated reduction of part of ceria at that low temperature, which is evident from the high H₂/Cu molar ratio. Although, the temperature at which Ce₁₋ₓPdₓO₂₋₀.5 (B) catalysts take up hydrogen is higher than that of the corresponding A catalysts, the amount of hydrogen taken up per palladium by the former is much higher than the latter. The high H₂/M ratio of B catalysts is due to the higher dispersion of M over the smaller crystallites compared to the A catalysts. The M–CeO₂ interaction is attributed to the formation of linkages of the type –Ce⁴⁺–O²⁻–M²⁺–, leading to Ce₁₋ₓMₓO₂₋₀.5 solid solution. The enhancement of redox property with smaller crystallite size is reflected in the catalytic activity of CeO₂ and Ce₁₋ₓMₓO₂₋₀.5 catalysts. Even pure CeO₂ shows higher CO oxidation activity. Metal ion substitution brings down the light off temperature drastically and hence M²⁺ is the active site for CO adsorption.

An important observation made here is the higher amount of metal ion substitution in CeO₂ when cerrous nitrate is employed as the precursor. Decrease in crystallite size seems to aid an increase in the solid solubility of M²⁺ ion in CeO₂. In our earlier studies, we had shown that ions are largely concentrated on the surface of the CeO₂ crystallites. This is to be expected since no stoichiometric compound between MO and CeO₂ is known. Hence, smaller amount of M²⁺ can be substituted for Ce⁴⁺ sites simultaneously creating oxide ion vacancies on the surfaces. Higher the surface area, higher amount of M²⁺ ions can be substituted over CeO₂. Surface concentration measurement of Cu in Ce₁₋ₓCuₓO₂₋₀.5 indicated that in 5 atom % Cu taken in the preparation, surface concentration of Cu is 38%. This means, Cu²⁺ ions are largely present on the surface layers of CeO₂ nano crystallites. For every Cu²⁺ ion substitution for Ce⁴⁺ ion, one oxide ion vacancy needs to be created. Ideally, 1 g of CeO₂ crystallites of 30 nm size has ~1×10¹⁰ Ce⁴⁺ ions on the surface. In 5 atom % Cu/CeO₂, 1 g contains ~2×10¹⁰ Ce⁴⁺ ions. Thus, not all the Cu²⁺ ions can be accommodated on the surface. Since only about 40% Cu is present on the surface, about 50% Cu taken would be in the bulk CeO₂. However, with 10 nm CeO₂ crystallites, the total Ce⁴⁺ ions per g is ~3×10¹⁰ and thus in principle, all the Cu ions can replace Ce⁴⁺ ions on the surface of CeO₂ crystallites. This is the reason for higher Cu ion...
substitution with smaller crystallite size. Since Cu$^{2+}$ ions are largely present on the surface of CeO$_2$ crystallites, a greater decrease in the lattice parameter of CeO$_2$ was not observed. Therefore, even 5 atom % Cu/CeO$_2$ is sufficient to provide a high concentration of surface Cu$^{2+}$ sites and hence no more than 5 atom % Cu substitution is needed for higher catalytic activity. Surface concentration of Cu$^{2+}$ is already saturated at 5 atom % Cu/CeO$_2$. Similar reasoning holds for the Ce$_{1-x}$Pd$_x$O$_{2.8}$ catalysts.

In the case of Ce$_{1-x}$Pd$_x$O$_{2.8}$ catalysts, we do not see any enhancement in surface concentration of Pd with the decreasing crystallite size, which means that the extra Pd goes to the bulk. The maximum surface enrichment takes place at 2 atom % substitution level. Also, this substitution is sufficient to achieve high catalytic activity as is observed for CO oxidation as well as NO reduction by CO.

Conclusions

The present study shows improvement of the redox as well as the catalytic activity of two important classes of catalysts, namely Ce$_{1-x}$Cu$_x$O$_{2.8}$ and Ce$_{1-x}$Pd$_x$O$_{2.8}$, over the same catalysts previously investigated, by merely changing the cerium precursor, and keeping all the other conditions the same. The findings have been substantiated by several techniques. The salient features of our investigations are: (i) precursor has a dramatic effect on the crystallite size. While ceric ammonium nitrate yields crystallites of 30-45 nm size, use of cerous nitrate leads to 10-15 nm nano-crystalline CeO$_2$ under the same reaction conditions in a single step combustion method. When copper is substituted for cerium, the size of Ce$_{1-x}$Cu$_x$O$_{2.8}$ catalysts follows the same trend whereas the size decreases by half from CeO$_2$ to Ce$_{1-x}$Pd$_x$O$_{2.8}$ catalysts; (ii) use of cerous nitrate in place of ceric ammonium nitrate increases the solid solubility of Cu$^{2+}$ ion in CeO$_2$ from 5-10 atom % in the former to 10-15 atom % in the latter. Solid solubility of Pd$^{2+}$ ion in CeO$_2$ is ~3 atom % with ceric ammonium nitrate and this increases to ~10 atom % when cerous nitrate is employed; (iii) smaller crystallites with higher oxidation defects show high oxygen storage capacity; (iv) smaller crystallites of both CeO$_2$, 5 atom % Cu/CeO$_2$ and 2 atom % Pd/CeO$_2$ show higher catalytic activity, much higher than that expected solely on the basis of the increase in surface area; (v) higher dispersion of the metal ions in smaller crystallites with well-defined structure having -M$^{2+}$-O-Ce$^{4+}$ - type of linkages enhances the redox property which is reflected in the catalytic activity.

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