Chapter 4

SYNTHESIS, CHARACTERIZATION AND ACTIVITY STUDIES
OF CeO$_2$; Pd/CeO$_2$ AND PdM/CeO$_2$ ($M$=Cu, Co, Ni)
NANOPARTICLES
Outline
In heterogeneous catalysis, the supported catalyst system is potentially advantageous compared to their unsupported form because they possess a high surface to volume ratio and reusability, ease of separation, and enhanced catalytic activity. As a result of these the surface area available for interaction with substrates is maximized, as long as the newly exposed surface is catalytically active. The choice of support plays a crucial role which must have high surface area, less agglomeration, easy availability and low cost. The extensive use of cerium oxide nanoparticles, more commonly nanoceria is a well explored catalytic material used for various engineering and biological applications [1-9]. Owing to their unique redox property, cerium can exists in either the free metal form or metal oxide form. Amongst the three oxidation states of cerium, +2, +3 and +4, the +2 state is rare and is observed in CeH₂, Ce₂ and CeS, and the most common compound of cerium is cerium(IV) oxide (CeO₂) [10]. The presence of oxygen vacancies or crystal defects in the Ce⁴⁺ population leads to the formation of Ce³⁺ state, cerium(III) oxide (Ce₂O₃) i.e. there exists a cycle between the cerous, cerium(III) and ceric, cerium(IV) oxidation states. This Ce⁴⁺/Ce³⁺ redox couple has been the main focus of researchers in the past era. The significance of this unique and biocompatible redox couple in catalysis is remarkable in a diverse way [11-14]. This multifunctional well-known rare earth material with prevalent applications in the fields of catalysis [15], electrochemistry [16], fuel cells [17], energy conversion [18] and optics [19] have received major consideration due to their repeatable redox cycles depending on the conditions and the environment. The high oxygen storage capacity (OSC) and low redox potential between Ce⁴⁺ and Ce³⁺ leads ceria to promote as a three-way catalyst (TWC) to reduce NOx emissions as well as convert harmful CO and hydrocarbons (HC) to the less harmful carbon dioxide [20-22]. The cerium(IV) oxide–cerium(III) oxide cycle itself is a two-step thermochemical water splitting process based on cerium(IV) oxide and cerium(III) oxide which makes them applicable in the field of hydrogen production [23-24].

In this chapter 4, we have discussed about the synthesis, characterization and activity of CeO₂, Pd/CeO₂ and PdM/CeO₂ (M=Cu, Co, Ni) nanoparticles for different reactions. The chapter is divided into three sections:
Chapter 4

I. **Section 4A** CeO$_2$ Nanoparticles and Their Radical Scavenging Activity.

II. **Section 4B** Pd/CeO$_2$ Nanoparticles for Room Temperature Chemo-selective Reduction of Nitroaromatics.

III. **Section 4C** Synthesis and Characterization of PdM/CeO$_2$ (M= Cu, Co, Ni) Nanoparticles and Their Catalytic Evaluation.
Section 4A: CeO$_2$ Nanoparticles and Their Radical Scavenging Activity

Section 4A of the chapter 4 describes the synthesis and characterization of CeO$_2$ nanoparticles by precipitation method using three precipitants, ammonium bicarbonate (CeO$_2$-A), sodium hydroxide (CeO$_2$-S) and ammonium oxalate (CeO$_2$-O) respectively. To evaluate the redox property of CeO$_2$, the radical scavenging activity of the synthesized ceria nanoparticles was explored for DPPH and hydroxyl radical by simple in-vitro spectrophotometric approach. A schematic representation of the present investigation is shown in the Scheme 4A.1.

Scheme 4A.1: Schematic representation of the synthesis of ceria nanoparticles and their radical scavenging activity.

4A.1 Results and Discussion

4A.1.1 Characterization of CeO$_2$ nanoparticles

Three different ceria nanoparticles (NPs), viz., CeO$_2$-O, CeO$_2$-A and CeO$_2$-S were first characterized by powder XRD to elucidate the crystalline structure of the CeO$_2$ NPs. Figure 4A.1 (a) presents the powder XRD patterns of different CeO$_2$ NPs. It is apparent that the particles crystallize as face-centered cubic structure with the cell parameter of 0.5411 nm and space group Fm3m which corroborate well with the JCPDS 43-1002. This is also consistent with the Debye-Scherrer formula, which shows that the crystallite size is inversely proportional to the full width at half maximum. The diffraction peaks observed at 2θ = 28.52, 38.37, 47.59, and 56.20° are assigned to (111), (200), (220) and (311) reflection planes, respectively of fcc-CeO$_2$. 


To examine the thermal stability, i.e. conversion steps for the CeO$_2$ precursors thermogravimetric analysis (TGA) was carried out. The TGA patterns of the three CeO$_2$ precursors are presented in Figure 4A.1(b). Two major weight loss steps are noticed in case of CeO$_2$-O. The first weight loss step occurs within 250 °C which could be attributed to the physical water evaporation and chemical dehydration. Major weight loss observed between 250 and 380 °C with weight loss of ~50% is due to the removal of counter ions into gases. CeO$_2$-A and CeO$_2$-S shows immediate weight losses significantly from ambient temperature to ca. 350 °C as shown in the Figure 4A.1(b). FTIR analysis was used to demonstrate the existence of various functional groups present in the precursor as well as CeO$_2$ samples. FTIR spectra for the uncalcined and calcined CeO$_2$-samples are shown in Figure 4A.1(c,d), respectively. Characteristics bands at 3360, 1610, 1320, 798 and 496 cm$^{-1}$ represent N–H stretching (asymmetric), C=O stretching, C–O stretching, N–H bending, and Ce–O stretching vibration of CeO$_2$-O samples, respectively. Similarly, the prominent peaks

Figure 4A.1: (a) XRD patterns, (b) TGA plots and FT-IR spectra of (c) uncalcined and (d) calcined CeO$_2$-O, CeO$_2$-A and CeO$_2$-S nanoparticles.
(Figure 4A.1c) at the region 3410, 2360, 1520, 1330, 1060 and 411 cm\(^{-1}\) are observed for CeO\(_2\)-A and CeO\(_2\)-S samples. The correlation of the FTIR spectra of the precursor and CeO\(_2\) supports the transformation of the precursors to the corresponding CeO\(_2\) structures, as observed from the shifting of peaks and concomitant structural changes after calcination at 350 °C.

**Figure 4A.2:** N\(_2\) adsorption/desorption isotherms and BJH pore size distribution curve (inset) for the as-synthesized CeO\(_2\) NPs; (a) CeO\(_2\)-O, (b) CeO\(_2\)-A and (c) CeO\(_2\)-S.

**Table 4A.1:** BET surface area, pore volume and pore size data of CeO\(_2\)-O, CeO\(_2\)-A and CeO\(_2\)-S nanoparticles

<table>
<thead>
<tr>
<th>CeO(_2) Sample</th>
<th>BET surface area (m(^2)g(^{-1}))</th>
<th>BJH cumulative pore volume (ccg(^{-1}))</th>
<th>Pore diameter (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO(_2)-O</td>
<td>236.8</td>
<td>0.256</td>
<td>3.7</td>
</tr>
<tr>
<td>CeO(_2)-A</td>
<td>59</td>
<td>0.022</td>
<td>3.6</td>
</tr>
<tr>
<td>CeO(_2)-S</td>
<td>33.3</td>
<td>0.005</td>
<td>3.6</td>
</tr>
</tbody>
</table>

To study the surface and textural property of the CeO\(_2\) NPs, N\(_2\) adsorption/desorption experiments were performed at liquid N\(_2\) temperature (−196 °C) using Brunauer-Emmett-Teller (BET) method. Figure 4A.2 presents adsorption/desorption isotherms of the as-synthesized ceria nanoparticles. The isotherms represents characteristic type IV hysteresis loop of H1 type which signify the mesoporous material. The BET surface area of CeO\(_2\)-O nanoparticles is found to be 236.8 m\(^2\)/g whereas CeO\(_2\)-A and CeO\(_2\)-S shows 59 and 33.3 m\(^2\)/g, respectively. It is interesting to note that the synthesized CeO\(_2\)-O nanoparticles exhibit very high BET surface area of 236.8 m\(^2\)/g,
which is much greater than previous literature reports [25-28]. At the same time the diameters of pores were also calculated using Barrett-Joyner-Halenda method (BJH method) and no significant difference is observed for the samples. The pore size distribution plots are displayed in the inset of the isotherms in the Figure 4A.2. Table 4A.1 shows the brief details of the surface and textural data related to BET surface area, pore volume and pore size various CeO$_2$ NPs. The diameter range suggests that particles are mesoporous in nature. The difference in surface area is observed which may be correlated to the complexation process by the different precipitating agents employed during the syntheses. Although all the samples have same pore size, but there is a vast difference in the pore volume of the samples for which difference in surface area is very high. In case of the ceria nanoparticles synthesized by using ammonium oxalate (CeO$_2$-O), the pore volume is particularly very high compared to the other two which eventually indicate the presence of larger number pores that result in the increase of surface area. This is might be due to the fact that during the complexation process of that particular sample, the development of the pores is quite high.

The excellent redox property and high oxygen storage capacity (OSC) of ceria makes it a very essential catalyst for many catalytic reactions. Raman spectroscopy is an available, non-destructive and significant analytical tool to investigate the intrinsic defect sites on nanoceria. And also the catalytic activity of the same can be correlated to their defect sites. Ceria has a cubic fluorite type lattice structure and belongs to the O$_h^5$ (Fm3m) space group. The Raman spectra for the two different CeO$_2$ samples were obtained using Ar$^+$ ion laser with a fundamental band at 514.5 nm. The power of each laser line was kept about 1 % of 20 mW to prevent local heating effects and the resolution of the spectrometer was 0.3 cm$^{-1}$. Figure 4A.3 shows the intensity versus Raman shift for the respective ceria samples. The peak at 462 cm$^{-1}$ is typically assigned to the F$_{2g}$ symmetrical stretching mode of Ce-O bond in the fluorite type lattice. Complementary two more weak bands are also noted at 591 and 266 cm$^{-1}$ due to the second order transverse acoustic (2TA) mode and defect-induced (D) mode [29, 30].
Figure 4A.3: Typical Raman spectra of (a) CeO$_2$-A, (b) CeO$_2$-O and (c) CeO$_2$-S nanoparticles; and the magnified Raman spectra of the respective samples (inset).

Figure 4A.4: XPS analysis of CeO$_2$ nanoparticles; core-level Ce 3d XP spectrum of (a) CeO$_2$-A; (b) CeO$_2$-S and (c) CeO$_2$-O and (d) core-level XP spectrum of O 1s of CeO$_2$-O NPs.

The D-band near 590 cm$^{-1}$ which is associated with oxygen vacancies in the cubic lattice relative to that of first order F$_{2g}$ peak. The growth of this band indicates creation of more oxygen vacancies and in tandem signifies the increase of Ce$^{3+}$ content in the
system. The activity of the samples can also be recognized from this feature, as the high content of Ce$^{3+}$ ion replicates more activity for the reaction. It could be observed from the Figure 4A.3 (inset) that the peak intensity for the D-band of CeO$_2$-O is slightly higher compared to the others, which signifies higher Ce$^{3+}$ content in the sample. Further the XPS analyses was also carried out to investigate the surface oxidation states of the elements present in the as-synthesized CeO$_2$ NPs. Figure 4A.4 shows the typical Ce 3d XP spectrum of CeO$_2$-A; CeO$_2$-S and CeO$_2$-O NPs. The Ce 3d region mainly assigned to Ce 3d$_{3/2}$ and Ce 3d$_{5/2}$ states. However, due to spin orbit coupling and photoemission effect, Ce 3d region further characterized into ten components. The figure shows the deconvoluted peaks of Ce 3d region for the two groups’ u and v. The components v$_0$ (881.1 eV), v’ (885.4 eV), u$_0$ (897.9 eV), u’ (903.9 eV) and v (884.4 eV), v’’ (889.4 eV), v’’’ (894.6 eV), u (901.0 eV), u’’ (907.4 eV), u’’’ (915.3 eV) corresponds to Ce$^{3+}$ and Ce$^{4+}$ species, respectively [31,32]. The deconvoluted peaks of O 1s for CeO$_2$-O are shown in Figure 4A.4(d). O 1s XP spectrum shows two major peaks O$_{ads}$ (531.6 eV) and O$_{lat}$ (529.2 eV), respectively. The O$_{lat}$ peak is the dominating which is due to lattice oxygen species (O$^{2-}$) of CeO$_2$. The O$_{ads}$ peak corresponds to the surface adsorbed oxygen due to the adsorption of –OH species and H$_2$O on the CeO$_2$ surface. The relative concentration of the Ce$^{3+}$ is calculated using the following equations, (1)-(3)

\[
\text{Ce}^{3+} = v_0 + v' + u_0 + u' \\
\text{Ce}^{4+} = v + v'' + u + u'' + u'''
\]

Relative concentration of Ce$^{3+}$ ($\%$) = \[ \frac{\text{Area (Ce}^{3+})}{\text{Area (Ce}^{3+}) + \text{Area (Ce}^{4+})} \times 100 \]

For the three different ceria samples the Ce$^{3+}$ content varies in the order CeO$_2$-O > CeO$_2$-A > CeO$_2$-S. The relative concentration of Ce$^{3+}$ is found to be highest in CeO$_2$-O (ca. 31.8 $\%$) whereas ca. 28.7 and 21.1 $\%$ for CeO$_2$-A and CeO$_2$-S respectively. Since from the Raman analysis also, it was revealed that CeO$_2$-O possess more Ce$^{3+}$ as the shoulder peak at 590 cm$^{-1}$ is quite intense compared to the other two ceria samples.
Figure 4A.5: SEM images of (a) CeO$_2$-O; (b) CeO$_2$-A and (c) CeO$_2$-S NPs.

Figure 4A.6: Representative (a) EDX pattern, (b) the electron image and EDS elemental maps of (c) Ce (d) O and (e) Ce+O in CeO$_2$-O nanoparticles, respectively.
The morphology and the surface structure of the nanoceria samples were examined by scanning electron microscopy (SEM) and energy dispersive X-ray (EDX) analyses. From the SEM images it is observed that the particles are within the nanometer range (Figure 4A.5) and agglomerate to form bigger aggregates. The porosity of the as-synthesized particles can also be defined from the images.

![Figure 4A.7](image)

**Figure 4A.7**: Transmission electron micrographs of CeO$_2$-O nanoparticles (a–e) at different resolutions and (f) histogram showing the distribution of particles.

The EDX analysis was also carried out to examine elemental composition of the synthesized particles and it shows that the only detectable elements present in the sample are Ce and O (Figure 4A.6). Moreover the EDS elemental mapping analysis of CeO$_2$-O clearly shows how the cerium and oxygen are distributed on the surface and
also confirms the purity of the sample by observing the absence of other elements. The elemental maps suggested good spatial dissemination of the elements present.

The CeO$_2$ nanostructures were further characterized by transmission electron microscopy (TEM) imaging. Figure 4A.7 presents the TEM and high-resolution TEM images of CeO$_2$-O NPs which clearly shows the formation of monodisperse CeO$_2$ particles with particle size of ca. 10 nm. The honeycomb like structure found in the figures (Figures 4A.7a-d) describes the existence of mesoporous spherical aggregates of cerium oxide NPs. The shapes of the particles are nearly spherical in nature and scattered in a homogenous manner. The lattice fringes having d-spacing of 0.31 nm (Figure 4A.7e) corresponds to that of (111) facet of CeO$_2$ as calculated using the relation given below:

$$d_{h,k,l} = \frac{\alpha}{\sqrt{h^2+k^2+l^2}} = \frac{5.412}{\sqrt{3}} = 0.312 \text{ nm}$$

This observation corroborate well with the XRD pattern (JCPDS 43-1002), i.e. (111) remains the preferred plane ($d = 0.31 \text{ nm}$) on the surface. The distribution of CeO$_2$ NPs is depicted in a histogram which is shown in Figure 4A.7(f). From the histogram it can be inferred that more than 90% of the NPs fall in the size range of 7–10 nm with an average size of 7.7 nm.

4A.1.2 DPPH scavenging activity

DPPH contains a nitrogen radical at the center of the molecule which exhibits an intense purple color due to absorption at 517 nm and its reduced form, 1,1-diphenyl-2-picrylhydrazyne (DPPH-H), shows a yellow color [33]. The DPPH radical scavenging ability of different CeO$_2$ NPs was evaluated. The control (DPPH without NPs) does not show any change with time in the absorption peak. In the presence of acetate buffer (pH 5.5) and CeO$_2$ NPs the color of DPPH solution gradually changes from deep violet to pale yellow as shown in Scheme 4A.2.
Scheme 4A.2: Structure and reaction scheme of scavenging DPPH radicals.

For this measurement the reaction was prolonged up to 60 min. With time the absorbance of the peak at 517 nm and 330 nm gradually decreases which attributed to the DPPH radicals. The percentage of DPPH scavenging can be estimated from the decrease of absorbance of peak at 517 nm, which represents the amount in the ethanol solution. The activity towards the scavenging property of each experimental CeO$_2$ samples examined regulating common environment. Figure 4A.8 presents the time dependent UV-visible absorption spectra of the reaction mixture after the addition of CeO$_2$-O, CeO$_2$-A and CeO$_2$-S, respectively.

Figure 4A.8: Time dependent UV-visible absorption spectra of DPPH scavenging by (a) CeO$_2$-O, (b) CeO$_2$-A and (c) CeO$_2$-S nanoparticles and (d) plot showing the DPPH % scavenging versus time (min).
Figure 4A.9: Time dependent UV-visible absorption spectra of DPPH scavenging by CeO$_2$-O nanoparticle under ultrasonic treatment.

Figure 4A.10: Comparison of % of DPPH scavenging by CeO$_2$-O nanoparticles with ultrasonic and without ultrasonic treatment.

The percentage of scavenging of each CeO$_2$ sample is calculated using the formula:

$$\text{DPPH scavenging (\%)} = \frac{(A_M - A_C)}{A_M} \times 100$$

where $A_M$ and $A_C$ are the absorbance of DPPH (control) and DPPH with the NPs at 517 nm, respectively. Figure 4A.8 (d) shows the DPPH scavenging (%) with time for the three different CeO$_2$ NPs. CeO$_2$-O exhibited better scavenging activity compared to the CeO$_2$-A and CeO$_2$-S. This might be due to their higher surface area and presence
of more oxygen vacancy sites which is related to more Ce\(^{3+}\) content in the synthesized CeO\(_2\)-O sample.

We have also investigated the antioxidant activity of CeO\(_2\)-O NPs, which is found to be best among three CeO\(_2\) NPs under the ultrasonic treatment. Figure 4A.9 shows UV-visible adsorption spectra of DPPH scavenging over CeO\(_2\)-O NPs under the influence of ultrasonic treatment. Sonication inside the water bath enhances DPPH scavenging activity of CeO\(_2\)-O NPs. The optimal conditions for ultrasonic treatment were 330 W of ultrasonic power at the tank temperature of 30 °C for 10 min of treatment time. Under this condition, the % of DPPH scavenging is remarkably found to almost 99% in 25 min which is considerably improved than that of without ultrasonic treatment. A comparative graph is presented in the Figure 4A.10. Thus, we can conclude that ultrasonic treatment enhances the DPHH scavenging activity which might be due to the mechanical effects that facilitate the reaction to be faster.

4A.1.3 Hydroxyl radical scavenging activity

The synthesized CeO\(_2\)-O NPs were also employed for hydroxyl free radical scavenging activity. Owing to their unique redox property ceria particles fluctuates in multiple oxidation states. The harmful hydroxyl radical (•OH) can be scavenged by CeO\(_2\) due to the presence of oxygen vacancy sites in its fluorite type lattice. For the generation of •OH radical we have chosen methyl violet (MV) as reagent which comprises a typical Fenton reaction where H\(_2\)O\(_2\) can be catalyzed by Fe\(^{2+}\) to produce the extremely reactive hydroxyl radical. Zhou and his co-workers reported how the generated hydroxyl radical can react with MV by attacking its \(-\text{C=O}\) where it has higher electron density of MV molecule [34]. An electrophilic addition takes place with the decrease in its maximum absorption. By investigating the change in the absorbance (denoted as ΔA) the amount of generated •OH can be estimated. Plot ‘a’ and ‘c’ in the Figure 4A.11 represents the UV-visible absorption spectra of individual MV solution and after the generation of •OH radical, respectively. MV shows a characteristic absorption peak at 582 nm, the absorbance of which is reduced due to the formation of reactive hydroxyl radical comprising the Fenton reaction. Hence, the generation of •OH radical is indirectly established. As the CeO\(_2\)-O sample was added
to the reaction mixture the maximum adsorption peak again raised up near to the absorbance of MV solution. This gives the evidence for scavenging of hydroxyl radical by the synthesized CeO$_2$-O. Thus, the antioxidant activity of CeO$_2$-O NPs towards hydroxyl free radical can be recognized.

![Figure 4A.11: UV-visible absorption spectra of (a) MV, (b) MV/FeSO$_4$/H$_2$O$_2$/CeO$_2$-O (ΔA=0.043), and (c) MV/FeSO$_4$/H$_2$O$_2$ (ΔA=0.453) solutions.](image)

Effect of concentration of CeO$_2$-O on •OH radical scavenging activity was also determined. For this, ΔA of the reactive solutions with different concentrations of CeO$_2$-O in longer incubation times were determined. Figure 4A.12 demonstrates the change in absorbance against incubation time for different concentrations of CeO$_2$. The decrease in ΔA means the improved scavenging activity of the respective particles. As it can be seen from figure, plot ‘a’ where CeO$_2$ concentration is 10 µM displays ΔA= 0.036 which is decreases to 0.011 in plot ‘b’ i.e. 50 µM CeO$_2$ by the incubation time 1 min. The value of ΔA at 6 min changes from 0.105 to 0.124 and 0.054, respectively (plots a, b, c). The ΔA values also decreases for higher incubation times, which indicate that higher concentrations of CeO$_2$ can eliminate more hydroxyl radical. To conclude with the increase of concentration, the hydroxyl radical scavenging ability of CeO$_2$-O is enhanced.
Figure 4A.12: Change of ΔA with incubation time when the CeO₂-O concentrations are (a) 10 µM, (b) 50 µM and (c) 100 µM, respectively.

In summary, cerium oxide nanoparticles were successfully synthesized using ammonium oxalate, ammonium bicarbonate and sodium hydroxide as precipitants. The surface valence state composition (Ce⁴⁺/Ce³⁺), morphology of nanoceria and the micro-environment of oxygen vacancy feature are attributed for the action against DPPH and hydroxyl free radical scavenging property for the cerium oxide nanoparticles. From the simple photometric study in-vitro, the role of DPPH and hydroxyl free radical scavenging activity of CeO₂ nanoparticles can be established.
Section 4B: Pd/CeO$_2$ Nanoparticles for Room Temperature Chemo-selective Reduction of Nitroaromatics.

In this section, Pd-nanoparticles stabilized on mesoporous cerium oxide (Pd/CeO$_2$) nanoparticles were synthesized and studied their catalytic activity for the reduction of substituted nitroaromatics using sodium borohydride as reductant. A schematic representation for the synthesis of Pd/CeO$_2$ nanoparticles is shown in the Scheme 4B.1. The catalyst shows excellent catalytic activity and chemoselectivity for the conversion of nitroaromatics into their corresponding amine derivatives at room temperature. A kinetic study explains that the reaction follows pseudo-first order kinetics.

Scheme 4B.1: Schematic representation showing the synthesis of Pd/CeO$_2$ NPs.

4B.1 Results and Discussion

4B.1.1 Structural Characterization

The Pd/CeO$_2$ nanoparticles (NPs) were synthesized by modified two step methodology. At first, the CeO$_2$ NPs were synthesized by conventional precipitation method using ammonium oxalate as precursor and after that Pd/CeO$_2$ were obtained under hydrothermal treatment. To determine the phase structure of as-synthesized nanoparticles powder XRD and the results are shown in Figure 4B.1. The characteristic diffraction peaks located at the $2\theta = 28.5$, 38.3, 47.5 and 56.2 ° corresponding to (111), (200), (220) and (311) crystal planes of cubic CeO$_2$ nanoparticles (JCPDS 43-1002). The diffraction patterns suggest that particles crystallize as fcc fluorite type lattice with a cell parameter of 0.5411 nm. XRD pattern of Pd (Figure 4B.1a) shows diffraction at $2\theta = 40.1$ ° which represents (111) crystalline plane of Pd nanoparticle (JCPDS 05-0681). Pd/CeO$_2$ nanoparticles shows
almost similar XRD pattern to that of the CeO$_2$ nanoparticles (Figure 4B.1 c). No characteristic diffraction peak was observed for Pd nanoparticles in Pd/CeO$_2$ catalyst system. This might be due to high dispersion or incorporation of metal nanoparticles to the support that is on the CeO$_2$ assembles. The diffraction peaks were intensive and moreover no other additional peaks were detected indicating high purity and good crystallinity of the sample.

**Figure 4B.1**: Powder X-ray diffraction patterns of as-synthesized (a) Pd, (b) CeO$_2$ and (c) Pd/CeO$_2$ nanoparticles.

The UV-Vis diffuse reflection spectrum (DRS) of CeO$_2$ nanoparticles is presented in Figure 4B.2. As expected, CeO$_2$ particles exhibited three adsorption maxima at ~255, 285 and 340 nm which are due to Ce$^{3+}$←O$^2$ charge transfer (255 nm); Ce$^{4+}$←O$^2$ (285) and inter band transitions (340 nm). To investigate the surface and textural property of the synthesized nanoparticles, N$_2$ adsorption/desorption
experiments were conducted. Figure 4B.3(a, b) displays the N\textsubscript{2} adsorption/desorption isotherms and BJH measurements for Pd, CeO\textsubscript{2} and Pd/CeO\textsubscript{2} nanoparticles, respectively. The isotherms of Pd/CeO\textsubscript{2} and Pd represents type IV hysteresis loop of H1 type which signifies the mesoporous material. Though, CeO\textsubscript{2} nanoparticles display N\textsubscript{2} adsorption/desorption isotherm that is combination of H1 and H2 hysteresis loop of type IV. Table 4B.1 summarizes BET surface area, BJH cumulative pore volume and pore diameter of the synthesized nanoparticles. The BET surface area and the pore diameter is found to highest in case of Pd/CeO\textsubscript{2} nanoparticle 384.1 m\textsuperscript{2}g\textsuperscript{-1} and 6.5 nm, respectively. This increased surface area of Pd/CeO\textsubscript{2} nanoparticles is might be due to the larger pores of Pd nanoparticles which couldn’t get into the surface of CeO\textsubscript{2} nanoparticle and thus increases the specific surface area of the sample.

**Figure 4B.3:** (a) N\textsubscript{2}-adsorption/desorption isotherm and (b) the BJH pore size distribution curve of synthesized Pd/CeO\textsubscript{2}, CeO\textsubscript{2} and Pd NPs, respectively.

**Table 4B.1:** BET surface area (m\textsuperscript{2}g\textsuperscript{-1}), BJH cumulative pore volume (cc g\textsuperscript{-1}) and Pore diameter (nm) of the synthesized nanoparticles

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>BET surface area (m\textsuperscript{2}g\textsuperscript{-1})</th>
<th>BJH cumulative pore volume (cc g\textsuperscript{-1})</th>
<th>Pore Diameter (nm)</th>
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<tr>
<td>1</td>
<td>Pd</td>
<td>110.8</td>
<td>0.216</td>
<td>4.1</td>
</tr>
<tr>
<td>2</td>
<td>CeO\textsubscript{2}</td>
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<td>3.66</td>
</tr>
<tr>
<td>3</td>
<td>Pd/CeO\textsubscript{2}</td>
<td>384.1</td>
<td>0.553</td>
<td>6.5</td>
</tr>
</tbody>
</table>
SEM analysis was performed to gain information about morphology of the synthesized catalyst. From the SEM image (Figure 4B.4a), some irregular shapes of the nanoparticles were observed which are self-assembled due to the agglomeration. Figure 4B.4 (b) represents the typical EDX pattern of the as-synthesized Pd/CeO$_2$ which shows the presence of detectable element Pd, Ce and O in the synthesized nanoparticle. No other elements were observed which confirms the purity of the sample. Further TEM analysis was accomplished for Pd/CeO$_2$ nanoparticles. Typical TEM images of the as-synthesized nanoparticles at different resolutions are shown in Figure 4B.5. The CeO$_2$ nanoparticles were highly porous monodisperse spherical aggregate with honeycomb like structure as discussed in the Section 4A. However, the particles have a great tendency toward agglomeration to form the bigger aggregates. Figure 4B.5 (a) and (b) presents the typical TEM image for Pd/CeO$_2$ NPs. They shows mostly spherical aggregates which are homogeneously distributed. It can be clearly seen from the figure that, Pd nanoparticles are well associated with CeO$_2$ nanoparticles having mostly spherical shape are uniformly arranged in them. The corresponding SAED pattern (Figure 4B.5c) taken from a small area; which represents some well-defined concentric rings generated from Pd/CeO$_2$ nanoparticles. The rings are assigned to various diffraction planes of cubic-CeO$_2$ nanoparticles. Furthermore, this observation reveals the polycrystalline nature of the particles. Also, the particle size distribution graph for the image (a) obtained by using Image J software is presented in Figure 4B.5(d). The histogram suggests that most of the particles fall in the diameter range of 3-5 nm.
To investigate the chemical states of the elements present, XPS analyses were performed. The obtained spectra are summarized in the Figure 4B.6. The core-level XP spectrum of Ce 3d is represented in the Figure 4B.6(a), from which six predominant peaks can be identified. The peaks located at the binding energies of 885.4 eV and 899 eV are the characteristic peaks of Ce$^{3+}$ whereas the peaks at 882.6 eV, 901 eV, 907.4 eV and 916.7 eV can be attributed to Ce$^{4+}$. This observation indicates the presence of both Ce$^{3+}$ and Ce$^{4+}$ ions in the synthesized nanocatalyst. The components of v and u i.e. v, v' and u$_0$, u, u', u'' are corresponds to Ce 3d$_{5/2}$ and Ce 3d$_{3/2}$ states respectively [35]. The core-level XP spectrum of O 1s is shown in Figure 4B.6(b). There are two main components in the region of O 1s; one is at the binding energy of 529.2 eV and other is at 531.6 eV.
Figure 4B.6: XPS analysis of Pd/CeO$_2$ nanoparticles; XP core level spectrum of (a) Ce 3d, (b) O 1s and (c) Pd 3d.

The peak located at 529.2 eV is arising due to the lattice oxygen species ($O_{\text{lat}}$) which is denoted as $O_{\text{lat}}$. The other peak at the higher binding energy 531.6 eV is denoted as $O_{\text{ads}}$, which is due to the adsorption of hydroxyl species on the catalyst surface [36]. Pd 3d region shows predominantly two major peaks at the binding energy of 335.2 and 340.9 eV respectively which corresponds to Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ species. However, Pd is present mostly Pd$^{0}$ state as the intensity of the peak at 335.2 eV is higher than that of the other. Nevertheless, the results demonstrate the formation of Pd/CeO$_2$ nanoparticles.

4B.1.2 Catalytic Activity

The catalytic property of the as-synthesized high surface area Pd/CeO$_2$ nanoparticles were investigated for the aqueous phase reduction of nitroaromatic compound. For instance, we have examined the reduction of 4-NP, which is a well-
known phenolic compound for its harmful carcinogenic and hazardous properties. On reduction, it gives 4-AP which is an important intermediate in various biological and synthetic processes. Reduction of 4-NP to 4-AP in presence of mild reducing agent NaBH₄ was tested by simple UV-Visible spectrophotometry. Aqueous solution of 4-NP exhibits a characteristic peak at 317 nm in the UV-visible absorption spectrum. After the addition of NaBH₄, the peak is red shifted to 400 nm due to the formation of 4-nitrophenolate ion (Figure 4B.7a). Colour of the solution is also changes from light yellow to dark yellow. Addition of catalyst to the reaction mixture causes decrease in the adsorption peak at 400 nm.

![Figure 4B.7: Time-dependent UV-Vis absorption spectra of the catalytic reduction of 4-NP to 4-AP; (a) showing the formation of nitrophenolate ion, over (b) Pd nanoparticles, (c) Pd/CeO₂ nanoparticles and (d) plot of ln(Aₐ/A₀) versus reaction time. Conditions: catalyst amount = 4 mg, [4-NP] = 0.1 mM and [NaBH₄] = 20 mM.](image)

Together with this, a shoulder peak at 298 nm is also observed which is characteristic peak of 4-AP and hence the reduction of 4-NP to 4-AP can be recognized. Reduction of 4-NP to 4-AP was carried out over unsupported monometallic Pd and Pd/CeO₂
nanoparticles to ensure the role of support on the catalytic activity. The progress of the reaction was monitored at different intervals of time. Figure 4B.7(b, c) represents the time dependent UV-visible adsorption spectra for the reduction of 4-NP to 4-AP over Pd and Pd/CeO$_2$ nanoparticles, respectively. It is interesting to note that, Pd/CeO$_2$ nanoparticles took only 8 min for the complete reduction of 4-NP to 4-AP whereas Pd nanoparticles needed 40 min to complete the reaction. Since, the amount of NaBH$_4$ is large excess compared to those of 4-NP and therefore the reaction mechanism is best described by taking pseudo-first order kinetics. The plot of ln(A$_t$/$A_0$) versus time gives good linear correlation as shown in the Figure 4B.7(d). The apparent rate constant values were calculated and found to be $7.1 \times 10^{-2}$ min$^{-1}$ and $62.3 \times 10^{-2}$ min$^{-1}$ over Pd and Pd/CeO$_2$ nanoparticles, respectively. As estimated, the supported nanocatalyst shows enhanced catalytic activity in terms of rate constant which is almost nine-fold greater than the unsupported one. Thus, it is clearly revealed that Pd nanoparticles stabilized on mesoporous CeO$_2$ nanomaterial has the potential to exhibit considerably enhanced catalytic activity for the reduction of 4-NP to 4-AP which may be attributed to preferential deposition of Pd nanoparticles on the more catalytically active sites of the support CeO$_2$.

Table 4B.2: Summary of Apparent rate constant ($k_{app}$), linear regression co-efficient ($R^2$) and the reduction time over different amount of Pd/CeO$_2$ nanoparticles for the reduction of 4-NP

<table>
<thead>
<tr>
<th>Sl No.</th>
<th>Amount of catalyst (mg)</th>
<th>Apparent rate constant ($k_{app} \times 10^{-2}$ min$^{-1}$)</th>
<th>$R^2$</th>
<th>Reduction time (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1</td>
<td>14.3</td>
<td>0.89</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>3</td>
<td>20.5</td>
<td>0.98</td>
<td>15</td>
</tr>
<tr>
<td>3</td>
<td>4</td>
<td>62.3</td>
<td>0.98</td>
<td>8</td>
</tr>
<tr>
<td>4</td>
<td>5</td>
<td>66.6</td>
<td>0.97</td>
<td>5</td>
</tr>
</tbody>
</table>

To examine the influence of catalyst dosages on the reduction behaviour, the reaction was carried out over four different amounts of catalyst, viz., 1, 3, 4 and 5 mg, keeping...
other parameters identical. Table 4B.2 summarizes the variation of apparent rate constant value, $R^2$ and the time of completion for the reduction of 4-NP to 4-AP over different amount of catalyst dosages. It is clearly evident from the table that by increasing the amount of catalyst there is a sharp increase in the apparent rate constant value and decrease in the reduction time. This is due to the presence of more catalytically active sites in the increased amount of catalyst.

![Figure 4B.8](image)

**Figure 4B.8:** Recyclability test for the reduction of 4-NP to 4-AP over Pd/CeO$_2$ nanoparticles. Conditions: catalyst amount = 4 mg, [4-NP] = 0.1 mM and [NaBH$_4$] = 20 mM.

In practical applications, catalyst recycling or reusability is very important for heterogeneous catalytic reactions. The recyclability test was carried out for the reduction of 4-NP over Pd/CeO$_2$ nanoparticles up to three consecutive cycles. After each cycle, the catalyst was collected from the reaction mixture by centrifugation and then washed with distilled water, dried, and applied for another cycle of the reaction. The percentage of conversion is calculated in each cycle using the relation

$$\text{% Conversion} = (1 - \frac{A_t}{A_0}) \times 100$$

Figure 4B.8 represents % conversion of 4-NP to 4-AP versus time (min) for three cycles. It is seen from the figure that up to the third cycle the conversion percentage is
greater than 80%, indicating the higher catalytic activity of the synthesized nanoparticle. The decrease in the activity after 3 cycles is observed due to loss of catalyst at each cycle. Moreover, the activity decreases due to the oxidation of the metal particles in contact with moisture present in the air.

**Scheme 4B.2:** Plausible reaction mechanism for the reduction of 4-NP to 4-AP using NaBH₄ as reducing agent.

A plausible reaction mechanism for the reduction of 4-nitrophenol in presence of sodium borohydride is proposed in the Scheme 4B.2. The reduction behavior of NaBH₄ and its decomposition on the catalyst surface has been extensively studied over last few years. Wunder *et al.* studied the reduction kinetics of 4-nitrophenol catalyzed by metallic nanoparticle and proposed a mechanistic pathway based on Langmuir-Hinshelwood model [37]. Similar investigation was achieved by Zhang *et al.* for the reduction of 4-nitrophenol over silver nanoparticles [38]. The reaction mechanism for this reduction reaction can be best described by “solution-diffusion mechanism”. First, sodium borohydride ionizes and gets adsorbed onto the catalyst surface followed by diffusion. Nitrophenol is also get adsorbed onto the catalyst surface and once both the substrate are chemisorbed, there is a hydrogen transfer from BH₄⁻ to nitrophenol. The nitrocompound is then reduced to nitroso compound and further to the corresponding hydroxylamine compound.
Table 4B.3: Summary of the room temperature reduction of different nitroaromatics over Pd/CeO\textsubscript{2} NPs \textsuperscript{a}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrate</th>
<th>Product</th>
<th>Time/min</th>
<th>Conversion \textsuperscript{b} (%) / Selectivity \textsuperscript{c} (%)</th>
</tr>
</thead>
</table>
| 1     | \begin{figure}[H]
|       | \begin{center}
|       | \includegraphics[width=0.2\textwidth]{1.png}
|       | \end{center}
|       | 1-chloro 3-nitrobenzene | \begin{center}
|       | \includegraphics[width=0.2\textwidth]{2.png}
|       | \end{center}
|       | 75 | 55 / > 90 |
| 2     | \begin{figure}[H]
|       | \begin{center}
|       | \includegraphics[width=0.2\textwidth]{3.png}
|       | \end{center}
|       | 4-nitrotoluene | \begin{center}
|       | \includegraphics[width=0.2\textwidth]{4.png}
|       | \end{center}
|       | 50 | 100 / > 99.9 |
| 3     | \begin{figure}[H]
|       | \begin{center}
|       | \includegraphics[width=0.2\textwidth]{5.png}
|       | \end{center}
|       | 4-nitrophenylamine | \begin{center}
|       | \includegraphics[width=0.2\textwidth]{6.png}
|       | \end{center}
|       | 70 | 85 / > 99.9 |
| 4     | \begin{figure}[H]
|       | \begin{center}
|       | \includegraphics[width=0.2\textwidth]{7.png}
|       | \end{center}
|       | 3-amino-4-nitroaniline | \begin{center}
|       | \includegraphics[width=0.2\textwidth]{8.png}
|       | \end{center}
|       | 60 | 99 / > 99.9 |
| 5     | \begin{figure}[H]
|       | \begin{center}
|       | \includegraphics[width=0.2\textwidth]{9.png}
|       | \end{center}
|       | 3-nitroaniline | \begin{center}
|       | \includegraphics[width=0.2\textwidth]{10.png}
|       | \end{center}
|       | 40 | 100 / > 99.9 |

\textsuperscript{a}Reaction conditions: nitrocompound 1.0 mmol, Pd/CeO\textsubscript{2} 15 wt\% of the substrate and NaBH\textsubscript{4} 5 mmol; \textsuperscript{b,c} Conversion and Selectivity determined by GC-MS.

The hydroxylamine, finally get reduced to the corresponding aniline derivative which is the rate determining step of the reaction. Taking the excellent performance of the Pd/CeO\textsubscript{2} nanoparticles towards the reduction of 4-nitrophenol, we have also investigated their efficacy for chemoselective reduction of various nitroaromatics. The catalytic activities of the nanoparticles were evaluated by taking freshly prepared nitro substrate with NaBH\textsubscript{4} as reducing agent in aqueous medium. The reaction occurred at room temperature and the reaction contents were kept stirring upto the specific time to complete the reaction. In the absence of catalyst, no reaction progress was observed.

Table 4B.3 summarizes the reaction results of the reduction of some nitro aromatic compounds over Pd/CeO\textsubscript{2} nanoparticles at room temperature. 1-chloro 3-nitrobenzene is converted to the desired amine product within 75 min with 55% conversion. (Table 4B.3, entry 1). However, 4-nitrotoluene is reduced to its ammine derivative with 100% conversion within the reduction time of 50 min only (Table 4B.3, entry 2).
Nitroanilines, especially 2, 3, and 4-nitroanilines were also found to give excellent conversion and selectivity (Table 4B.3, entry 3-5). Though, among the nitroanilines, 4-nitroaniline is found to be very active which gives 100% conversion with 99.9% selectivity within 40 min only. This might be due to the fact that 4-nitroaniline is resonance stabilized and therefore the intermediate forms will be the most stable compared to the others due to the delocalization of the negative charge on the oxygen atom. All the reaction products were analyzed by GC-MS after the completion of the reaction. The methodology provides remarkably a general procedure for the chemoselective reduction of –NO$_2$ group with high conversion and selectivities.

In conclusion, we have successfully synthesized the cerium oxide supported palladium nanoparticles by a modified two-step methodology. The obtained Pd/CeO$_2$ nanoparticles perform enhanced catalytic activity towards the reduction of various nitroaromatics using NaBH$_4$ as a reducing agent. The catalyst system is found to be very effective towards the reduction reaction as it catalyzes the reaction at room temperature with efficient chemoselectivity. To study the kinetic performance, UV-Visible spectrophotometric analysis were also performed for the reduction of 4-nitrophenol; which shows the reaction follows pseudo-first order kinetics with an apparent rate constant ($k_{app}$) value of $62.3 \times 10^{-2}$ min$^{-1}$. The catalyst is found to remain active without any significant loss in activity after the third cycle of reaction. Thus, the present work suggests a simple, economically feasible chemical route to synthesize very active, reusable, environmentally friendly catalyst for the reduction of nitroaromatics at room temperature.
Section 4C: Synthesis and Characterization of PdM/CeO$_2$ (M= Cu, Ni, Co) Nanoparticles and Their Catalytic Evaluation.

In this Section 4C, porous CeO$_2$ stabilized PdM (M=Cu, Ni, Co) nanoparticles are synthesized by a modified hydrothermal method and their catalytic activities were evaluated for reduction of different water pollutants such as organic dyes and nitroaromatics. Catalytic studies show that the synthesized PdCu/CeO$_2$ nanoparticles can efficiently reduce model azo dyes, methyl orange (MO) and congo red (CR) with good recyclability. Among various PdCu compositions, Pd$_1$Cu$_9$/CeO$_2$ exhibits superior catalytic activity towards reductive degradation of MO and CR at room temperature. Thus, Pd$_1$Ni$_9$/CeO$_2$ and Pd$_1$Co$_9$/CeO$_2$ nanoparticles were also studied for the reduction of nitroaromatics at room temperature.

4C.1 Results and Discussion

4C.1.1 Structural Characterization of the synthesized Pd$_x$Cu$_{10-x}$/CeO$_2$ nanoparticles

A series of Pd$_x$Cu$_{10-x}$/CeO$_2$ (x=1, 2, 3) nanoparticles (NPs) were synthesized by modified two step methodology. At first, the CeO$_2$ NPs were synthesized by conventional precipitation method using ammonium oxalate as precursor compound and after that different composition of PdCu/CeO$_2$ were obtained under hydrothermal treatment. To determine the phase structure of as-synthesized nanoparticles powder XRD analysis was performed. Figure 4C.1 shows the powder XRD pattern of Cu/CeO$_2$, Pd/CeO$_2$, Pd$_1$Cu$_9$/CeO$_2$ and CeO$_2$ nanoparticles. The diffraction peaks located at $2\theta = 28.5, 38.3, 47.5$ and $56.2^{\circ}$ are indexed to (111), (200), (220) and (311) reflections of cubic CeO$_2$ nanoparticles (JCPDS 43-1002), respectively. The diffraction patterns show that particles crystallize as face-centred cubic lattice with a cell parameter of 0.5411 nm. XRD pattern of Pd$_1$Cu$_9$/CeO$_2$ nanoparticles is similar to that of the CeO$_2$ nanoparticles which is because of the high dispersion or incorporation of metal nanoparticles into the support that is on the CeO$_2$ assemblies. Identical results are found in case of Pd/CeO$_2$ nanoparticles. No characteristic diffraction peaks are observed for the metallic particles indicating high dispersion and low loading of the metallic particles over the CeO$_2$ support. However, Cu/CeO$_2$ nanoparticles show a strong diffraction peak at $2\theta = 43.3^{\circ}$ which corresponds to (111) reflection of copper according to the JCPDS 04-0836.
Figure 4C.1: Powder XRD patterns of (a) Cu/CeO$_2$ (b) Pd/CeO$_2$ (c) Pd$_{1}$Cu$_{9}$/CeO$_2$ and (d) CeO$_2$ nanoparticles.

Figure 4C.2: (a) SEM image and (b) EDX pattern for Pd$_{1}$Cu$_{9}$/CeO$_2$ nanoparticles.

The morphology and the elemental composition of the Pd$_{1}$Cu$_{9}$/CeO$_2$ nanoparticles are further examined by SEM and EDX analyses. Figure 4C.2 (a) and (b) show the typical SEM and EDX pattern of as-synthesized Pd$_{1}$Cu$_{9}$/CeO$_2$ nanoparticles, respectively. As it could be observed from the SEM image that the particles agglomerate to form bigger particles and distributed homogenously. The TEM images of both as-synthesized CeO$_2$
and Pd\textsubscript{1}Cu\textsubscript{9}/CeO\textsubscript{2} nanoparticles are displayed in Figure 4C.3. CeO\textsubscript{2} nanoparticles demonstrate the formation of highly porous monodispersed spherical aggregates with honeycomb like structure. A high resolution TEM image of CeO\textsubscript{2} clearly shows lattice fringe with d-spacing of about 0.31 nm, which corresponds to (111) facets of CeO\textsubscript{2}. This observation corroborates well with the XRD pattern i.e. (111) remains the preferred plane (d = 0.31 nm) on the surface. Figure 4C.3 (c, d) shows typical TEM images of Pd\textsubscript{1}Cu\textsubscript{9}/CeO\textsubscript{2} nanoparticles which are self-assembled into spherical porous fcc-CeO\textsubscript{2} assemblies. As displayed, the particles are homogeneously distributed on the surface with a tendency to get agglomeration. The HRTEM image of Pd\textsubscript{1}Cu\textsubscript{9}/CeO\textsubscript{2} (Figure 4C.3 d) exhibits the presence of many spherical aggregates on the surface. It can be observed from the figure that the metal nanoparticles are highly dispersed on the catalyst support.

**Figure 4C.3:** TEM images of (a,b) CeO\textsubscript{2} nanoparticles and (c,d) Pd\textsubscript{1}Cu\textsubscript{9}/CeO\textsubscript{2} nanoparticles at different resolutions.
Figure 4C.4: XP spectrum of Pd$_1$Cu$_9$/CeO$_2$ nanoparticles; (a) wide-scan survey, (b) Ce 3d, (c) O 1s, (d) Pd 3d and (e) Cu 2p core level XP spectrum.

To determine the oxidation states of the elements present in the as-synthesized catalyst, XPS analysis was accomplished as shown in Figure 4C.4. The wide scan survey spectrum (Figure 4C.4 a) shows the presence of cerium, oxygen, palladium and copper in Pd$_1$Cu$_9$/CeO$_2$ nanocatalyst. Figure 4C.4 (b) shows the typical signals of Ce 3d spectrum which are mainly due to Ce 3d$_{5/2}$ and Ce 3d$_{3/2}$. Due to their spin-orbit splitting and photo emission effect Ce 3d region further categorized into ten components of two groups ‘v’ and ‘u’ corresponding to various Ce$^{3+}$ and Ce$^{4+}$. The ‘v’ components are v$_0$, v, v’, v'', v''' located at the binding energy of 881.1, 883.2, 886.3, 889.6 and 899.4 eV, respectively represent Ce 3d$_{5/2}$ contributions. Similarly the ‘u’ components i.e. u$_0$, u, u', u'' and u''' at the binding energy of 900.2, 901.8, 904.6, 908.3
and 917.6 eV respectively shows Ce 3d3/2 contributions. The presence of all these peaks clearly reveals the presence of both Ce3+ and Ce4+ in the synthesized nanocatalyst [39]. Figure 4C.4 (c) shows O 1s XP spectrum with two major peaks at the binding energy ca. 529.2 and 531.6 eV. The peak at the higher binding energy side (~531.6 eV) can be ascribed to the surface adsorbed oxygen denoted as O$_{ads}$ which is due to the adsorption OH species on the catalyst surface. The subsequent peak at lower binding energy side (~529 eV) denoted as O$_{lat}$ is due to the lattice oxygen species (O$_2^-$) on the ceria support [31]. The core-level XP spectrum of Pd 3d and Cu 2p are presented in Figure 4C.4 (d) and (e), respectively. The noticed two major peaks at the binding energy of 335.2 and 340.9 eV of Pd 3d region are mainly due to Pd 3d3/2 and Pd 3d5/2 species, respectively [40]. The deconvolution of the Pd 3d spectrum shows that Pd is present mostly in the Pd$^0$ state (~335 eV) rather than Pd$^{2+}$ (~336.9 eV). Cu 2p core-level XP spectrum shows that Cu 2p$_{3/2}$ and Cu 2p$_{1/2}$ species are located at the binding energy of 932.3 and 952.1 eV, respectively. The predominant Cu 2p$_{3/2}$ peak observed at the binding energy ~932 eV can be attributed to zero-valent Cu [41].

4C.1.2 Catalytic Activity Studies

4C.1.2.1 Reductive Degradation of Methyl Orange

To investigate the catalytic performance of the synthesized nanoparticles reductive degradation of two azo dyes, methyl orange (MO) and congo red (CR) were studied using NaBH$_4$. An aqueous solution of MO exhibits absorption peak at 462 nm in UV-visible spectra. When an aqueous solution of NaBH$_4$ was added to MO solution, no obvious change in the absorbance can be visibly observed. This indicates that MO is not reduced in an effective way by only NaBH$_4$. However, after the addition of the catalyst, the spectral band at 462 nm gradually decreases and a small shoulder peak at 252 nm gradually increases which is assigned to the hydrazine derivative of the dye molecule. This suggests that the synthesized nanoparticles were responsible for the plausible cleavage of –N=N– double bond as the chromophoric group of azo dye structure and hence decolorizing the solution. The reaction mechanism can be explained by electron relay via metal nanoparticles. The catalyst system accepts electron from the donor BH$_3$OH$^-$. When NaBH$_4$ is added to the reaction mixture, the hydride form BH$_4^-$ may be trapped by the nanoparticles and adsorbed on their surface and transfers electron to the catalyst. Negatively charged nanoparticles then released
the electron to the acceptor molecule (dye) produced their reduced form. Figure 4C.5 (a)-(e) shows the time dependent UV-visible adsorption spectra of the reaction solution over Cu/CeO₂, Pd/CeO₂, Pd₁Cu₆/CeO₂, Pd₂Cu₈/CeO₂ and Pd₃Cu₉/CeO₂, respectively. It is worth mentioning that amongst the catalysts tested the reduction reaction proceeds much faster over the bimetallic supported catalysts compared to the monometallic counterparts. FTIR analyses of MO and degraded product demarcate the absence of functional groups present in the parent MO as presented in Figure 4C.6.

**Figure 4C.5:** Time-dependent UV-visible absorption spectra of the catalytic degradation of MO over (a) Cu/CeO₂, (b) Pd/CeO₂, (c) Pd₁Cu₆/CeO₂, (d) Pd₂Cu₈/CeO₂ and (e) Pd₃Cu₉/CeO₂ and (f) plot of $A_t/A_0$ Vs. reaction time. Conditions: catalyst amount = 4 mg, [MO] = 10 mg/L and [NaBH₄] = 20 mM.
Figure 4C.6: FT-IR analysis of methyl orange (MO) and its degraded product.

Table 4C.1: Summary of apparent rate constant ($k_{app}$), linear regression co-efficient ($R^2$) value and time of completion for the reductive degradation of MO over various catalysts

<table>
<thead>
<tr>
<th>S. No.</th>
<th>Catalyst</th>
<th>$k_{app}$ ($\times 10^{-2}$ min$^{-1}$)</th>
<th>$R^2$</th>
<th>Time of completion (min)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>No catalyst</td>
<td>0.46</td>
<td>0.94</td>
<td>Not completed</td>
</tr>
<tr>
<td>2</td>
<td>Cu/CeO$_2$</td>
<td>2.73</td>
<td>0.90</td>
<td>&gt;60</td>
</tr>
<tr>
<td>3</td>
<td>Pd/CeO$_2$</td>
<td>3.18</td>
<td>0.92</td>
<td>&gt;60</td>
</tr>
<tr>
<td>4</td>
<td>Pd$_1$Cu$_9$/CeO$_2$</td>
<td>10.18</td>
<td>0.98</td>
<td>15</td>
</tr>
<tr>
<td>5</td>
<td>Pd$_2$Cu$_9$/CeO$_2$</td>
<td>8.45</td>
<td>0.99</td>
<td>30</td>
</tr>
<tr>
<td>6</td>
<td>Pd$_3$Cu$_9$/CeO$_2$</td>
<td>5.73</td>
<td>0.96</td>
<td>40</td>
</tr>
<tr>
<td>7</td>
<td>CeO$_2$</td>
<td>1.44</td>
<td>0.98</td>
<td>Not completed</td>
</tr>
</tbody>
</table>

This improved catalytic activity of bimetallic supported catalysts might be due to their bifunctional or synergistic effect of the two metals present. Variation of $A_t/A_0$ with respect to time for MO reduction over all the catalysts is shown in Figure 4C.5 (f). It
should be also noted that without the addition of catalyst or in presence of only CeO₂, there was no appreciable change in the absorbance of MO in the UV-visible spectra. Time-dependent UV-visible adsorption spectra of the catalytic degradation of MO without the addition of catalyst and only CeO₂ are presented in Figure A17, Appendix I. Table 3C.1 summarizes the apparent rate constant ($k_{app}$), linear regression coefficient ($R^2$) and reduction time for all the catalysts. The reaction kinetic is assumed to be pseudo-first order as the concentration of sodium borohydride is relatively larger than the dye solution and presume to remain constant during the reaction. Thus pseudo-first order kinetics can be applied to estimate the rate constant. Plot of $\ln \left( \frac{A_t}{A_0} \right)$ versus reduction time shows a linear correlation and from the slope of the graph the apparent rate constant can be calculated. Figure 4C.7 shows the plots of $\ln \left( \frac{A_t}{A_0} \right)$ versus reduction time for the CeO₂ stabilized bimetallic PdCu nanoparticles of different compositions. The best $k_{app}$ is found to be $10.18 \times 10^{-2}$ min⁻¹ for Pd₉Cu₁/CeO₂ catalyst. For comparison, the reduction $k_{app}$ of the control experiment was also calculated without the addition of catalyst and it was found to be $0.46 \times 10^{-2}$ min⁻¹ (Table 4C.1, S.-No. 1). It could be inferred that synthesized nanoparticles accelerated the reductive degradation of MO with increasing the $k_{app}$ depending on various composition of PdCu stabilized on CeO₂.

![Figure 4C.7: Plot of $\ln \left( \frac{A_t}{A_0} \right)$ versus time for the catalytic degradation of MO over Pd₉Cu₁/CeO₂, Pd₈Cu₂/CeO₂ and Pd₇Cu₃/CeO₂ catalyst.](image)

Although the Pd₉Cu₁/CeO₂ exhibits high catalytic activity for the degradation of MO, in view of practical applications, it is of great significance to investigate recyclability of Pd₉Cu₁/CeO₂. To test the recyclability of the catalyst, six successive cycles of
catalytic degradation were carried out employing 4 mg catalyst and 20 mM NaBH₄. Since the catalyst was heterogeneous in nature, so it was collected from the reaction mixture by centrifugation. The collected Pd₁Cu₉/CeO₂ catalyst was washed with distilled water, dried, and applied for another cycle of the reaction. The percentage of degradation is calculated in each cycle using the relation

\[
\% \text{ Degradation} = (1 - \frac{A_t}{A_0}) \times 100
\]

Figure 4C.8: Recyclability of Pd₁Cu₉/CeO₂ for the catalytic degradation of MO. Conditions: catalyst amount = 4 mg, [MO] = 10 mg/L and [NaBH₄] = 20 mM.

Figure 4C.8 presents the degradation (%) of MO for six consecutive cycles. As it could be observed from the figure that the reductive degradation of MO was still higher than 74% even after six successive cycles, clearly indicates that the Pd₁Cu₉/CeO₂ exhibits excellent reusability. The reason for decrease in catalytic activity may be small loss of catalyst during separation. Nevertheless, the catalyst exhibits not only high efficiency but also shows good recyclability for MO degradation reaction, which is highly promising for practical applications involved in the treatment of dye-containing wastewater. The corresponding time dependent UV-visible absorption spectra of the recyclability test for catalytic degradation of MO over Pd₁Cu₉/CeO₂ nanoparticles along with plot of ln (A_t/A_0) vs. reaction time are presented in Figure A18, Appendix I.
Figure 4C.9: Variation of apparent rate constant ($k_{\text{app}}$) towards catalytic degradation of MO over Pd$_1$Cu$_9$/CeO$_2$ employing different (a) concentration of NaBH$_4$ and (b) amount of catalyst.

To eliminate the effect of adsorption during the degradation of dyes we have also examined the degradation efficiency of our best catalyst i.e. Pd$_1$Cu$_9$/CeO$_2$, for the reductive degradation of MO. Figure A19, Appendix I shows the time-dependent UV-visible adsorption spectra and the % degradation efficiency of MO in presence of the only catalyst with respect to time. As it can be seen from the figure that, very little amount of MO (around 2%) is adsorbed by Pd$_1$Cu$_9$/CeO$_2$ which is remain constant after 60 min. To study the effect of concentration of reducing agent and amount of catalyst, the reaction was carried out over different NaBH$_4$ concentrations and various amounts of catalyst employing the best catalyst, i.e. Pd$_1$Cu$_9$/CeO$_2$. The reaction was investigated by using five different concentrations of NaBH$_4$ in the range 20-60 mM with 4 mg of Pd$_1$Cu$_9$/CeO$_2$. Figure 4C.9 (a) shows the variation of $k_{\text{app}}$ with NaBH$_4$ concentrations. It can be observed from the figure that up to 50 mM NaBH$_4$, there was no appreciable change in the rate constant. However at 60 mM NaBH$_4$ there is a sharp increase in the $k_{\text{app}}$. Similarly, to investigate the influence of catalyst amounts, the reaction was carried out over five different amounts of Pd$_1$Cu$_9$/CeO$_2$ in the mass range 2-6 mg with 20 mM NaBH$_4$. As observed from Figure 4C.9 (b), the $k_{\text{app}}$ increases with increasing catalyst amount. The variation of $k_{\text{app}}$ is not significant up to 5 mg of catalyst; however it increases enormously over 6 mg of catalyst. The $k_{\text{app}}$ increases ca. 6-fold. The increase in the $k_{\text{app}}$ on increasing the catalyst amount is due to the presence
of catalytically increased active surface for reaction. The corresponding UV-visible absorption spectra for catalytic degradation of MO over Pd₁Cu₉/CeO₂ in the presence of various NaBH₄ concentrations and catalyst amounts are presented in Figures A20 and A21, respectively in the Appendix I.

4C.1.2.2 Reductive Degradation of Congo Red

For the wide applicability of the best catalyst, Pd₁Cu₉/CeO₂ catalytic degradation of another model azo dye congo red (CR) was also studied. It is an anionic dye with two –N=N– bonds, widely used in textiles, wood pulps, paper and plastic industries. However, it is found that, it inhibits neurotoxic effects of human pancreatic amyloidiogenic peptide amylin. Therefore its degradation is enormously important.

Figure 4C.10: (a) Time-dependent UV-visible absorption spectra and (b) linear plot of ln (Aₜ/A₀) versus time for the catalytic degradation of CR over Pd₁Cu₉/CeO₂.

Figure 4C.10 (a) and (b) shows the time dependent UV-Visible adsorption spectra and the linear plot of ln (Aₜ/A₀) versus time for the catalytic degradation of CR over Pd₁Cu₉/CeO₂, respectively. CR exhibits two adsorption bands at 498 and 350 nm in aqueous medium. These bands are associated with the azo group and corresponds to the π→π* and n→π* transitions, respectively. After the addition of NaBH₄ and the catalyst to the reaction mixture, a gradual decrease in these two absorption bands are observed, which indicate the catalytic degradation of the dye. The degradation reaction follows pseudo-first order kinetics with respect to CR, because concentration of NaBH₄ is much larger than that of CR. Apparent rate constant (k_{app}) was calculated
from the linear plot of ln(A_t/A_0) versus reduction time. The adsorption capacity of the only catalyst is also examined which is somewhat larger (around 14%) compared to that of MO. The time dependent UV-visible adsorption spectra and plot of % degradation versus time for CR is presented in the Figure A22 in the Appendix I.

**Figure 4C.11:** Variation of apparent rate constant ($k_{app}$) towards catalytic degradation of CR over Pd$_1$Cu$_9$/CeO$_2$ employing different (a) concentration of NaBH$_4$ and (b) amount of catalyst.

To study the effect of NaBH$_4$ concentration and amount of catalyst, the degradation reaction was also carried out over [NaBH$_4$] in the range 20-60 mM and amount of catalyst in the mass range 2-6 mg employing Pd$_1$Cu$_9$/CeO$_2$. Figure 4C.11 (a, b) presents the variation of $k_{app}$ over different concentration of NaBH$_4$ and amount of catalyst, respectively. It is evident from Figure 4C.11 (a) that $k_{app}$ increases with increasing concentration of NaBH$_4$. Figure 4C.11 (b) shows that the $k_{app}$ is highest for 4 mg of Pd$_1$Cu$_9$/CeO$_2$. It might be because, over this amount of catalyst successful effective collisions occurred by lowering the activation energy of the reaction and simultaneously increasing the rate constant. The corresponding UV-visible absorption spectra for catalytic degradation of CR over Pd$_1$Cu$_9$/CeO$_2$ in the presence of various NaBH$_4$ concentration and catalyst amount are presented in Figures A23 and A24, respectively in the Appendix I.
4C.1.3 Characterization of Pd\textsubscript{1}Ni\textsubscript{9}/CeO\textsubscript{2} and Pd\textsubscript{1}Co\textsubscript{9}/CeO\textsubscript{2} nanoparticles

Pd\textsubscript{1}Ni\textsubscript{9}/CeO\textsubscript{2} and Pd\textsubscript{1}Co\textsubscript{9}/CeO\textsubscript{2} NPs were synthesized by using similar methodologies that we have used for Pd\textsubscript{1}Cu\textsubscript{9}/CeO\textsubscript{2}. Powder XRD analysis was performed to determine the phase structure of as-synthesized nanoparticles. Figure 4C.12 shows the powder XRD pattern of Pd\textsubscript{1}Ni\textsubscript{9}/CeO\textsubscript{2} and Pd\textsubscript{1}Co\textsubscript{9}/CeO\textsubscript{2} nanoparticles, respectively. The diffraction peaks represents the crystalline planes of cubic CeO\textsubscript{2} nanoparticles as we have already discussed earlier (4C.1.2). The high dispersion or incorporation of metal nanoparticles into the support that is on the CeO\textsubscript{2} assemblies results for this kind of observation. No characteristic diffraction peaks are observed for the metallic particles indicating high dispersion and low loading of the metallic particles over the CeO\textsubscript{2} support.

![XRD patterns](image)

**Figure 4C.12:** XRD patterns of (a) Pd\textsubscript{1}Ni\textsubscript{9}/CeO\textsubscript{2} and (b) Pd\textsubscript{1}Co\textsubscript{9}/CeO\textsubscript{2} NPs respectively.

EDX analysis was performed to investigate the elements that present in the synthesized catalyst. Figure 4C.13 (a) and (b) represents the typical EDX pattern of as-synthesized Pd\textsubscript{1}Ni\textsubscript{9}/CeO\textsubscript{2} and Pd\textsubscript{1}Co\textsubscript{9}/CeO\textsubscript{2} NPs, respectively. The presence of the desired elements could be observed from the EDX analysis. Figure 4C.13 (c)-(f) shows the EDS elemental maps for Pd, Ni, Ce and O of Pd\textsubscript{1}Ni\textsubscript{9}/CeO\textsubscript{2} NPs. Similarly Figure 4C.13 (g)-(j) shows the EDS elemental maps for Pd, Co, Ce and O of Pd\textsubscript{1}Co\textsubscript{9}/CeO\textsubscript{2} NPs respectively which represents the spatial dissimilation of the elements on the catalyst surface.
Figure 4C.13: EDX pattern of (a) Pd$_1$Ni$_9$/CeO$_2$ and (b) Pd$_1$Co$_9$/CeO$_2$ NPs and the EDS-elemental maps of Pd, Ni, Ce, O (c-f) for Pd$_1$Ni$_9$/CeO$_2$ and Pd, Co, Ce, O (g-j) for Pd$_1$Co$_9$/CeO$_2$ NPs, respectively.

Figure 4C.14: (a-c) TEM images at different resolutions and (d) SAED pattern of Pd$_1$Ni$_9$/CeO$_2$ NPs.
Figure 4C.15: TEM images at different resolution (A-E) and the SAED pattern (F) of Pd\textsubscript{1}Co\textsubscript{9}/CeO\textsubscript{2} NPs.

The TEM images of both as-synthesized Pd\textsubscript{1}Ni\textsubscript{9}/CeO\textsubscript{2} and Pd\textsubscript{1}Co\textsubscript{9}/CeO\textsubscript{2} NPs are displayed in Figure 4C.14 and 4C.15, respectively. A high resolution TEM image of Pd\textsubscript{1}Ni\textsubscript{9}/CeO\textsubscript{2} clearly shows homogeneous dispersion of the metallic nanoparticles on CeO\textsubscript{2} support. From the image (c) well defined lattice fringes can be seen at the 2 nm scale. The SAED pattern represents some bright spots from which the polycrystalline nature of the sample can be recognized. Figure the 4C.15 shows typical TEM images of Pd\textsubscript{1}Co\textsubscript{9}/CeO\textsubscript{2} nanoparticles at different resolution which are self-assembled into spherical porous fcc-CeO\textsubscript{2} assemblies. The presence of many spherical aggregates on the surface can be observed from the TEM images. The image (d) in the Figure 4C.15
shows how the PdCo bimetallic nanoparticles are supported on CeO$_2$ (the bigger crystal with d-spacing of 0.30 nm). The particles crystallize with well-defined lattice planes which are clearly seen from the image (e). The polycrystallinity of the sample can be recognized from the SAED pattern (Figure 4C.15f) which appears with bright spots.

Moreover, XPS analysis was also performed to investigate the oxidation states of the elements present in the as-synthesized catalysts. Figure 4C.16 shows the XPS of Pd$_1$Ni$_9$/CeO$_2$ NPs. The presence of Ce 3d, O 1s, Pd 3d and Ni 2p in the synthesised catalyst can be remarked from their core-level XP spectra. Ce 3d shows the typical signals (Figure 4C.16 a) which are mainly due to Ce 3d$_{5/2}$ and Ce 3d$_{3/2}$, respectively. O 1s XP spectrum shows two major peaks at the binding energy ca. 529.2 and 531.6 eV which are mainly due to O$_{lat}$ respectively. The presence of Pd 3d$_{5/2}$ and Pd 3d$_{3/2}$ can be remarked (Figure 4C.16 c) from the core-level XP spectrum of Pd 3d.

**Figure 4C.16:** XPS analysis of Pd$_1$Ni$_9$/CeO$_2$ NPs; the core-level XP spectrum of (a) Ce 3d (b) O 1s (c) Pd 3d and (d) Ni 2p, respectively.
Figure 4C.16 (d) shows the core-level Ni 2p XP spectrum which shows two major peaks at the binding energy of 856.4 and 873.4 eV corresponds to Ni 2p\(_{3/2}\) and Ni 2p\(_{1/2}\), respectively. Figure 4C.17 represents the XPS analysis of Pd\(_{1}\)Co\(_{9}\)/CeO\(_{2}\) NPs. Similar observations can be noticed for core-level Ce 3d and O 1s species. Due to their spin-orbit splitting and photo emission effect Ce 3d region further categorized into ten components of two groups ‘v’ and ‘u’ corresponding to various Ce\(^{3+}\) and Ce\(^ {4+}\). As in the earlier cases, Pd 3d region exhibits two major peaks at the binding energy of 335.2 and 340.9 eV due to the Pd 3d\(_{5/2}\) and Pd 3d\(_{3/2}\) species, respectively. The core-level Co 2p XP spectrum (Figure 4C.17 d) shows two predominant peaks at the binding energy of 782.1 and 796.0 eV and which corresponds to Co 2p\(_{3/2}\) and Co 2p\(_{1/2}\). After deconvolution, together with them two more peaks at 785.6 and 803.5 eV are also noticed which are assigned to Co\(^{2+}\) species. Nevertheless, the results demonstrates the formation of Pd\(_{1}\)Ni\(_{9}\)/CeO\(_{2}\) and Pd\(_{1}\)Co\(_{9}\)/CeO\(_{2}\) NPs.

**Figure 4C.17**: XPS analysis of Pd\(_{1}\)Co\(_{9}\)/CeO\(_{2}\) NPs; the core-level XP spectrum of (a) Ce 3d (b) O 1s (c) Pd 3d and (d) Co 2p, respectively.
4C.1.4 Catalytic activity of Pd\textsubscript{1}Ni\textsubscript{9}/CeO\textsubscript{2} and Pd\textsubscript{1}Co\textsubscript{9}/CeO\textsubscript{2} nanoparticles

To investigate the catalytic activity of the synthesized Pd\textsubscript{1}Ni\textsubscript{9}/CeO\textsubscript{2} and Pd\textsubscript{1}Co\textsubscript{9}/CeO\textsubscript{2} NPs, reduction of 4-NA was carried out using NaBH\textsubscript{4} as a reducing agent. 4-NA maximum adsorption peak at 381 nm which on reduction gradually decreases with simultaneous appearance of two more peaks at 240 and 300 nm. These two peaks are due to the formation of p-phenylenediammine (PPD). We have investigated the reaction over Pd\textsubscript{1}Ni\textsubscript{9}/CeO\textsubscript{2} NPs at room temperature. Time dependent UV-visible spectra for the reduction of 4-NA are shown in Figure 4C.18.

Figure 4C.18: (a) Time dependent UV-visible absorption spectra, (b) plot of ln (A\textsubscript{t}/A\textsubscript{0}) vs. Time, (c) plot of A\textsubscript{t}/A\textsubscript{0} vs. time for each cycle and (d) plot of % conversion and time for each cycle for the reduction of 4-NA over Pd\textsubscript{1}Ni\textsubscript{9}/CeO\textsubscript{2} NPs. Conditions: [4-NA] = 0.1 mM, [NaBH\textsubscript{4}] = 20 mM, catalyst amount = 4 mg.

The corresponding ln (A\textsubscript{t}/A\textsubscript{0}) plot vs. time is shown in Figure 4C.18 (b). The reaction kinetics can be described as ln (A\textsubscript{t}/A\textsubscript{0}) = −k\textsubscript{app}t, in which k\textsubscript{app} is the apparent rate constant and t is the reaction time. A\textsubscript{t} and A\textsubscript{0} are the absorbances of 4-NA at time t and 0 respectively. To test the recyclability of the catalysts, we have carried out the reduction of 4-NA employing 4 mg catalyst upto eight consecutive cycles. The plot of
$A_t/A_0$ vs. time at each cycle is shown in the Figure 4C.18 (c). The percentage of conversion at each is calculated and plotted against time in the Figure 4C.18 (d). The catalyst was quite stable up to forth cycle, giving rise to > 90% conversion. However, some loss in the conversion is noticed after fifth cycle which might be due to the loss of catalyst during the separation at each cycle.

**Figure 4C.19:** (a) Time dependent UV-visible absorption spectra and the plot of ln $(A_t/A_0)$ vs. time (inset); (b) plot of % conversion and time for each cycle for the reduction of 4-NA over Pd$_1$Co$_9$/CeO$_2$ NPs. Conditions: [4-NA] = 0.1 mM, [NaBH$_4$] = 20 mM, catalyst amount = 4 mg.

**Table 4C.2:** Summary of apparent rate constant ($k_{app}$), linear regression co-efficient ($R^2$) value and time of completion for the reduction of 4-NA over various catalysts.

<table>
<thead>
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<th>Sl. No.</th>
<th>Catalyst</th>
<th>$k_{app} \times 10^{-2}$ min$^{-1}$</th>
<th>$R^2$</th>
<th>Time of completion (min)</th>
</tr>
</thead>
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<tr>
<td>1</td>
<td>Pd/CeO$_2$</td>
<td>5.87</td>
<td>0.90</td>
<td>30</td>
</tr>
<tr>
<td>2</td>
<td>Ni/CeO$_2$</td>
<td>0.621</td>
<td>0.95</td>
<td>&gt; 60</td>
</tr>
<tr>
<td>3</td>
<td>Co/CeO$_2$</td>
<td>2.07</td>
<td>0.90</td>
<td>&gt; 60</td>
</tr>
<tr>
<td>4</td>
<td>Pd$_1$Ni$_9$/CeO$_2$</td>
<td>27.6</td>
<td>0.99</td>
<td>12</td>
</tr>
<tr>
<td>5</td>
<td>Pd$_1$Co$_9$/CeO$_2$</td>
<td>26.29</td>
<td>0.99</td>
<td>11</td>
</tr>
</tbody>
</table>
Figure 4C.19 (a) shows the time dependent UV-visible spectra for the reduction of 4-NA over Pd$_{1}$Co$_{9}$/CeO$_{2}$ NPs. The reaction took almost 11 min to complete. The plot of ln ($A_t/A_0$) vs. time is shown in the inset of Figure 4C.19(a). The recyclability of the catalyst was also tested for six consecutive cycles. Figure 4C.19 (b) shows the plot of percentage of conversion at each cycle with respect to time for the reduction of 4-NA over Pd$_{1}$Co$_{9}$/CeO$_{2}$ NPs. To compare the results with monometallic catalysts supported on ceria, i.e., over Pd/CeO$_{2}$, Ni/CeO$_{2}$ and Co/CeO$_{2}$ we have also carried out the reaction over them and summarized the data in the Table 4C.2.

In conclusion, PdCu/CeO$_{2}$ nanoparticles with different composition of Pd and Cu (1:9, 2:8 and 3:7) were successfully synthesized via a modified hydrothermal method. The obtained PdCu/CeO$_{2}$ nanoparticles exhibit remarkable catalytic activity towards the catalytic degradation of organic dyes in presence of a mild reducing agent, NaBH$_{4}$. The reactions are found to be very effective and followed pseudo first-order kinetics. PdCu/CeO$_{2}$ nanoparticles are found to be stable because they produce little waste and successively recycled up to six consecutive cycles without significant loss of activity. These Pd$_{1}$Cu$_{9}$/CeO$_{2}$ nanoparticles might be applicable as nanomaterial for the use of environmental safety applications. Motivated by this, we have also synthesized Pd$_{1}$Ni$_{9}$/CeO$_{2}$ and Pd$_{1}$Co$_{9}$/CeO$_{2}$ nanoparticles and characterized them by various spectroscopic and analytical techniques. The catalytic activity of the catalysts were investigated for the reduction of 4-nitroaniline, a common nitro present in waste water. The catalysts show improved catalytic activity for the reduction reaction which is very much promising in the field of waste water treatment.

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Chapter 4


