Chapter - 6: Synthesis, characterization and photocatalytic study of cerium oxide/zeolite-NaX

6.1. Introduction

Various photocatalysts like TiO$_2$, ZnO, WO$_3$, CeO$_2$, and ZrO$_2$ nanoparticles are used for degradation of organic dyes [1,2]. Out of these catalysts, CeO$_2$ nanoparticles have been proven to be competent photocatalysts for environmental applications because of their strong redox ability, nontoxicity, long-term stability, and low cost [3]. Various methods available to prepare CeO$_2$ nanoparticles include hydrothermal, solvothermal, co-precipitation, sol-gel, solution combustion, and sonochemical methods.

CeO$_2$ nanoparticles are interesting due to their wide variety of applications in polishing agents, sunscreens, solid electrolytes, solar cells, fuel cells, phosphorescent/luminescent materials, photocatalysis, sensors, oxygen pumps, and metallurgy [4]. These applications take advantage of cerium high thermodynamic affinity for oxygen and sulfur, its potential redox chemistry involving Ce$^{III}$/Ce$^{IV}$ and the unique and useful absorption/excitation energy bands associated with its electronic structure [5]. Cerium is a lanthanide series rare earth element and exists as a free metal or oscillates between the Ce$^{III}$ and Ce$^{IV}$ oxidation states. Nano ceria (cerium oxide nanoparticles) also hop between Ce$^{III}$ and Ce$^{IV}$ valence states and they contain oxygen vacancies that allow the nanoparticles to act as regenerative catalysts [6].
Presently there is a growing interest in using coal fly ash derived zeolite for adsorption and degradation of dyes. The incorporation of light-absorbing transition metal heteroatoms in the framework of zeolites could make the structure photoactive [7]. Most of the previous studies reported the degradation of dyes using metal ions supported commercial zeolite and registered a high catalytic activity [8,9,10]. Pouretedal et al. [11] modified nanosized MCM-41/MCM-48 with CeO$_2$ impregnation and used the material for photocatalytic degradation of Congo red.

In the present work zeolite is first prepared from the waste material coal fly ash and then CeO$_2$ is incorporated into it. The resulting nano CeO$_2$/Zeo-NaX photocatalyst is assessed for its visible light activity by the photocatalytic degradation of brilliant green (BG), methylene blue (MB), methyl orange (MO) and p-Nitroaniline (p-NA). The results show that the developed zeolite photocatalyst material is in nano form and has greater efficiency in BG and MB pollutant degradation.

6.2. Experimental

6.2.1. Synthesis of CeO$_2$/zeolite-NaX

About 2 g of (NH$_4$)$_2$Ce(NO$_3$)$_6$ and 1 g of Zeo-NaX (Ch-3 Sec- 3.2.2) were dispersed in 30 ml of water and gently stirred at 333 K for 2 h. The obtained and Ce$^{4+}$ incorporated Zeo-NaX was filtered through whatman No.1 filter paper, washed thoroughly with distilled water and finally dried at 353 K overnight. Lastly the sample was calcined at 550$^\circ$ C for 4 h, in order to obtain ceria-incorporated zeolite (CeO$_2$/Zeo-NaX) material. The dried catalyst was ground into a fine powder and stored in zip-lock polythene cover with label for further characterization followed by their application as photocatalyst.
6.2.2 Characterization of the synthesized materials

FTIR spectra of the powdered zeolite samples were recorded using Jasco FTIR spectrophotometer model 410 in the wavenumber range 400–4000 cm\(^{-1}\) with a resolution of 2 cm\(^{-1}\). X-ray diffraction (XRD) was recorded for 20 = 10–80º in a step of 0.05º using PANalytical Expert Pro-MPG with generator set at 30 mA and 40 kV and Cu Kα radiation (λ = 1.5406 Å). The chemical composition of the synthesized materials was analyzed by wavelength dispersive X-ray fluorescence spectroscopy (XRF) (ASM 100 T). SEM images of the samples were observed with Jeol JSM-6390 instrument operating at 20 kV after coating the samples with gold. The samples were characterized by BET surface area analysis by nitrogen adsorption at 77K using an ASAP-2010 Porosimeter by Micromeritics Corporation. Diffuse reflectance spectra were recorded with UV–vis spectrophotometer, Shimadzu model UV-2550 against BaSO\(_4\) white background. The degradation products of MB, MO and p-NA were analyzed by Alliance 2795 HPLC coupled with LC/MSD Trab XCT ion-trap mass spectrometer. The solvent used as mobile phase was acetonitrile: 0.01 M ammonium acetate (pH 6.8) 30:70 vol/vol). The mass range was from 100 to 500 m/z.

6.3. Results and Discussion

6.3.1. FTIR characterization of the samples

The FTIR spectra of the synthesized materials are presented in Fig. 6.1. The spectrum of Na-X zeolite (Fig. 6.1b) exhibits absorptions at 461, 565, 674, 754 and 980-1200 cm\(^{-1}\) (broad band). The band in the region 980 - 1200 cm\(^{-1}\) represents the characteristic asymmetric stretching of Si–O–Al tetrahedral silica framework and Si-O-Si silica framework in the formed zeolite [12]. The weak band at 1646 cm\(^{-1}\) arises from the bending mode of water molecules. All these characteristic vibrations confirm the formation of zeolite (Zeo-NaX) on alkali treatment of fly ash [13,14].
The spectrum of CeO$_2$/Zeo-NaX (Fig.6.1c) exhibits the characteristic peaks at 433, 465, 533, 741, 1018 and 1634 cm$^{-1}$. This shows the blue shift in the characteristic peaks of Na-X zeolite by 5-10 cm$^{-1}$ upon CeO$_2$ incorporation [14]. That means Ce has some influence on the zeolite framework. Thus the IR spectra provide evidence for Zeo-NaX and CeO$_2$/Zeo-NaX materials and confirm their synthesis.

![FTIR spectra](image)

**Figure 6.1.** FTIR spectra of (a) fly ash, (b) Zeo-NaX, (c) CeO$_2$/Zeo-NaX and (d) CeO$_2$/Zeo-NaX-S

**6.3.2. Powder XRD characterization of the samples**

Powder XRD patterns of the prepared photocatalysts are displayed in Fig. 6.2. In Fig. 6.2a fly ash shows the diffraction peaks at $2\theta = 26.50^\circ$, $39.30^\circ$ and $40.78^\circ$ [15]. In Fig. 6.2b the presence of diffraction peaks at $2\theta = 15.47^\circ$, $23.37^\circ$ $26.72^\circ$, $31.03^\circ$ and $51.70^\circ$ (JCPDS card No. 39-0218) confirms the formation of Na-X crystals in the fly ash derived zeolite. X-ray diffraction pattern with broad signals given in Fig. 6.2c confirm the formation of nano CeO$_2$ through peaks at $2\theta = 29.20^\circ$, $48.39^\circ$ and $57.93^\circ$ (JCPDS card no. 31-0325). Crystallite size values (Table 6.1) support the inference of
ceria formation. The low intensity peaks represent the less crystalline nature of CeO\textsubscript{2}. The zeolite peaks are not distinctly seen in both fresh and spent CeO\textsubscript{2}/Zeo-NaX (Fig. 6.2c & 6.2d). This shows the formation of CeO\textsubscript{2} layer over the formed zeolite framework. Thus IR spectra and XRD patterns confirm the formation of zeolite materials (Zeo-NaX, and CeO\textsubscript{2}/Zeo-NaX) from coal fly ash.

**Figure 6.2.** PXRD patterns of (a) fly ash (b) Zeo-NaX (c) CeO\textsubscript{2}/Zeo-NaX and (d) CeO\textsubscript{2}/Zeo-NaX-S

**Table 6.1.** XRD data of fly ash, Zeo-NaX and CeO\textsubscript{2}/Zeo-NaX

<table>
<thead>
<tr>
<th>Material</th>
<th>2-theta (°)</th>
<th>d-spacing (Å)</th>
<th>FWHM (°)</th>
<th>Crystallite size (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>26.50</td>
<td>3.36</td>
<td>0.200</td>
<td>39.7</td>
</tr>
<tr>
<td>Zeo-NaX</td>
<td>26.72</td>
<td>3.33</td>
<td>0.133</td>
<td>59.8</td>
</tr>
<tr>
<td>CeO\textsubscript{2}/Zeo-NaX</td>
<td>33.40</td>
<td>3.05</td>
<td>1.873</td>
<td>4.40</td>
</tr>
</tbody>
</table>

**6.3.3. XRF Analysis**

**Table 6.2.** Chemical composition (Wt %) of Zeo-NaX and CeO\textsubscript{2}/Zeo-NaX derived from XRF analysis.
Table 6.2 presents the chemical composition of zeolite materials, derived from XRF analysis. As can be seen from Table 4.2 Ce$^{4+}$ ion exchange has substantially removed Na$_2$O by substituting with CeO$_2$. Other metal oxides have also undergone considerable decrease in their content increasing the proportion of CeO$_2$ (~36%). This reveals that major portion of the CeO$_2$ is placed at the surface of the material. Thus the synthesis process of CeO$_2$/Zeo-NaX material is confirmed and validated by XRF analysis.

6.3.4. SEM analysis of the samples

The SEM images of the prepared materials are displayed in Fig. 6.3. Fly ash particles are predominantly spherical in shape (Fig. 6.3a) with relatively smooth surface and few micron sizes. The prepared zeolite NaX image (Fig. 6.3b) shows the presence of fine spherical nano size (~100 nm) primary particles [13]. As observed in
image c, CeO\textsubscript{2}/Zeo-NaX has morphology similar to Zeo-NaX (image b) except some agglomeration leading to bigger secondary particles. That means CeO\textsubscript{2} incorporation through the pores of Zeo-NaX does not alter the morphology of zeolite material but facilitates agglomeration. The elemental analysis data of SEM EDX given in Table 6.3 clearly suggest the presence of required elements and the chemical composition of the materials. The Si/Al ratio is conserved in the formed zeolite from fly ash. The presence of 12.45 atomic % of Ce confirms the encapsulation of CeO\textsubscript{2} layer in the zeolite material.

**Figure 6.3.** SEM images of (a) fly ash, (b) Zeo-NaX, (c) CeO\textsubscript{2}/Zeo-NaX and (d) CeO\textsubscript{2}/Zeo-NaX-S
Table 6.3. Elemental composition of the materials from SEM EDX analysis

<table>
<thead>
<tr>
<th>Material</th>
<th>Element content (atomic %)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Si</td>
</tr>
<tr>
<td>Fly ash</td>
<td>15.77</td>
</tr>
<tr>
<td>Zeo-NaX</td>
<td>14.06</td>
</tr>
<tr>
<td>CeO$_2$/Zeo-NaX</td>
<td>12.21</td>
</tr>
<tr>
<td>CeO$_2$/Zeo-NaX-S</td>
<td>11.73</td>
</tr>
</tbody>
</table>

6.3.5. Surface area characterization

Figure 6.4. BET isotherms of (a) fly ash, (b) Zeo-NaX and (c) CeO$_2$/Zeo-NaX

The BET isotherms of the synthesized catalysts are shown in Fig. 6.4 and Table 6.4. Fly ash exhibits an incomplete adsorption desorption isotherm (Fig. 6.4a) with very low surface area 0.79 m$^2$/g. The formation of zeolitic structure in Zeo-NaX created type III isotherm and loading of CeO$_2$ modifies the isotherm into type II. The
formation of zeolite structure increased the surface area of fly ash (0.79 m²/g) to 28.72 m²/g. The addition of CeO₂ in the zeolite structure followed by its calcination improved the surface area considerably to 94.58 m²/g. Similar is the trend with pore volume. But pore sizes are reduced, perhaps due to the occupation of pores by Na⁺ in zeolite and later by CeO₂.

Table 6.4. Surface area, pore volume and pore size of zeolite materials

<table>
<thead>
<tr>
<th>Material</th>
<th>Surface area (m²/g)</th>
<th>Pore volume (cm³/g)</th>
<th>Pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fly ash</td>
<td>0.795</td>
<td>0.002</td>
<td>161.33</td>
</tr>
<tr>
<td>Zeo-NaX</td>
<td>28.72</td>
<td>0.163</td>
<td>101.96</td>
</tr>
<tr>
<td>CeO₂/Zeo-NaX</td>
<td>94.58</td>
<td>0.176</td>
<td>31.98</td>
</tr>
</tbody>
</table>

6.3.6. Diffuse reflectance spectral study

Figure 6.5. DRS of (a) fly ash, (b) Zeo-NaX, (c) CeO₂/Zeo-NaX and (d) CeO₂/Zeo-NaX-S
Diffuse reflectance spectra (DRS) of the materials are plotted in Fig. 6.5 and the band gap energy ($E_g$) values are obtained from the average of both direct and indirect band gap energies (Sec. 3.24.3, Ch-3). Fly ash exhibits a band gap value ($E_g$) of 2.59 eV which is increased on the formation of zeolite (3.08 eV). The synthesized CeO$_2$/Zeo-NaX system has a lower $E_g$ value of 1.95 eV due to the incorporation of CeO$_2$ particles in zeolite. The spent catalyst CeO$_2$/Zeo-NaX-S having a marginal effect of lower $E_g$ value (1.92 eV) suggests the stable nature of the synthesized system. The DRS study clearly shows that Zeo-NaX synthesized from coal fly ash is a poor visible light absorbing material while CeO$_2$ incorporation and zeolite conversion to CeO$_2$/Zeo-NaX greatly enhances its visible light absorption.

### 6.3.7. Visible light degradation of BG dye over different catalysts

The preliminary reactions were performed with 10 ppm of BG dye in the presence of 100 mg catalyst and the degradation data are given in Table 6.5. The degradation of BG is low (32.2 %) in the absence of light (dark-self degradation). Presence of light enhances the self degradation to 40.9 % with H$_2$O$_2$. However the presence of zeolite (Zeo-NaX) inhibits the self-degradation of BG down to 26.8 %. This shows that the zeolites itself is not a photocatalyst but functions as an adsorbent and protects BG from degradation. But with CeO$_2$ and CeO$_2$/Zeo-NaX degradation of BG is very much enhanced (more than two times compared to light) due to catalytic effect. Between the above two, CeO$_2$/Zeo-NaX has the higher efficiency and is the optimum catalyst. These results unequivocally demonstrate that all the constituents, catalyst, light, H$_2$O$_2$ etc., are required for maximum degradation of BG dye.
Figure 6.6. Visible light degradation of BG over different catalysts

Table 6.5. Visible light degradation of BG over different catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Dark</td>
<td>32.2</td>
</tr>
<tr>
<td>Light</td>
<td>40.9</td>
</tr>
<tr>
<td>Zeo-NaX</td>
<td>26.8</td>
</tr>
<tr>
<td>CeO$_2$</td>
<td>85.9</td>
</tr>
<tr>
<td>CeO$_2$/Zeo-NaX</td>
<td>94.8</td>
</tr>
</tbody>
</table>

Reaction condition: [BG] = 10 ppm (200 ml), Catalyst amount = 100 mg, Time = 3 h, pH = 6.9

6.3.8. Effect of reaction parameters on the degradation of BG dye

The study of effect of reaction parameters was performed by varying catalyst amount from 25 to 100 mg, dye concentration from 10 to 50 mg/l and pH from 4 to 10. The results are discussed in following sections.
6.3.8.1. Effect of catalyst amount

The effect CeO$_2$/Zeo-NaX of catalyst loading was studied from 25 to 100 mg maintaining other optimized parameters (dye concentration = 10 ppm) at natural pH. From Fig. 6.7, it is noted that the degradation efficiency increases, of course, marginally with increase in the amount of catalyst. The values of % of degradation are 77.24 %, 78.97 %, 85.78 % and 94.81 % for 25, 50, 75 and 100 mg respectively. This may be due to an increase in the active sites available on the catalyst surface for the reaction.

![Figure 6.7 Effect of catalyst loading](image)

6.3.8.2. Effect of dye concentration

Fig. 6.8 clearly depicts the dependence of dye concentration on the degradation efficiency of the catalyst CeO$_2$/Zeo-NaX. As the initial concentration is increased, the amount of BG degraded is also increased. The values of % degradation are 9.4%, 17.6%, 25.7%, 32.1% and 41.2% for 10 ppm, 20 ppm 30 ppm 40 ppm and 50 ppm.
respectively. At fixed catalyst dose (100 mg), the amount of dye molecule adsorption on catalyst may go down with increase in initial dye concentration. However, the observed enhancement in amount of dye degradation may have the origin in the following phenomena reported in previous works [16, 17]. Colored dye molecules in principle can improve the activity of catalyst via dye sensitization. In addition, it inhibits recombination of $e^-h^+$ pair by increasing the charge separation and thus increases the efficiency of the photocatalytic process.

Figure 6.8. Effect of dye concentration

6.3.8.3. Effect of pH

The pH is one of the most important factors for controlling the degradation of dye. The pH of brilliant green solution was adjusted in the range of 4 to 10 by adding HCl and NaOH (0.05 M) [18]. The reaction was carried out with acidic pH 4.1, neutral natural pH 6.9 and alkaline pH 10 keeping the amount of catalyst (100 mg), and dye concentration (10 ppm) as constant and the data are depicted in Fig. 6.9. The
percentage of BG degradation at this experimental condition is 28.98%, 94.81 % and 100 % at pH 4.1, 6.9 and 10.0 respectively. An increase in pH of the medium increases the degradation efficiency. This may be due to the generation of more OH radicals at higher pH by the reaction between OH⁻ ions and hole (h+) of the semiconductor [19].

![Graph showing percentage of degradation over time at different pH levels]

**Figure 6.9. Effect of pH**

### 6.3.8.4. Reuse of catalyst

The CeO₂/Zeo-NaX used in the photocatalytic process was filtered, washed with water and dried at 80 °C in a hot air oven and calcined at 550°C for 4 h before it was reused as such in the succeeding photocatalytic experiment. The fresh CeO₂/Zeo-NaX exhibited 94.81 % degradation efficiency and the first recycled CeO₂/Zeo-NaX-S shows 75.45 % degradation efficiency in 3 h (Fig. 6.10). Therefore it is clear that the photocatalyst CeO₂/Zeo-NaX can be reused without any drastic change in its catalytic activity. The considerable retainment of photoactivity in used/spent
CeO$_2$/Zeo-NaX catalyst could be explained by the maintenance of chemical, physical and morphological characteristics of the material even after two uses. The FTIR spectrum (Fig. 6.1d), XRD pattern (Fig. 6.2d), SEM image (Fig. 6.3d) and elemental composition (Table. 6.3) all confirm this statement, because these characteristics of the spent catalyst CeO$_2$/Zeo-NaX-S are similar to those of fresh catalyst. Only in Ce content, a deviation/decline is noticeable with spent catalyst (Table 6.3).

Figure 6.10. Effect of recycling the catalyst
6.3.9. Comparative photocatalytic degradation efficiency of fly ash derived CeO$_2$/Zeo-NaX towards Methylene blue, Methyl orange and p-Nitroaniline

**Figure 6.11.** Visible light degradation of (a) MB (b) MO and (c) p-NA

Reaction condition: [MB] or [MO] or [p-NA] = 10 ppm (200 ml), Catalyst amount = 100 mg, Time = 3 h, pH = 6.9, $\text{H}_2\text{O}_2 = 2$ ml

Apart from BG dye, the catalyst CeO$_2$/Zeo-NaX was employed to degrade other relevant dyes/compounds, MB, MO and p-NA at optimised condition. Fig. 6.11 and Table 6.6 present the data. The presence of CeO$_2$/Zeo-NaX photocatalyst is found effective for MB degradation (nearly twice as that of light*) and ineffective for MO and p-NA. Among the three pollutants taken for degradation, i.e. MB, MO and p-NA, the catalyst CeO$_2$/Zeo-NaX degrades only the cationic charged MB and the efficiency is nearly twice. BG is also a cationic dye for which the catalyst has 94.8%
degradation. For anionic dye and neutral p-NA, the catalyst is ineffective. The reason for this has already been discussed in Ch. 5.

**Table 6.6.** Visible light degradation of MB, MO and p-NA

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Degradation (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>MB</td>
</tr>
<tr>
<td><strong>Dark</strong></td>
<td>13.1</td>
</tr>
<tr>
<td><strong>Light</strong></td>
<td>21.8</td>
</tr>
<tr>
<td><strong>Light</strong>*</td>
<td>30.3</td>
</tr>
<tr>
<td><strong>Zeo-NaX</strong>*</td>
<td>18.6</td>
</tr>
<tr>
<td><strong>Ce-oxide/Zeo-NaX</strong>*</td>
<td>62.7</td>
</tr>
</tbody>
</table>

Reaction condition: [MB] or [MO] or [p-NA] = 10 ppm (200 ml), Catalyst amount = 100 mg, Time = 3 h, pH = 6.9, *H₂O₂ = 2 ml

**6.3.10. Comparison of degradation efficiencies of present and reported catalysts**

Table 6.7 presents a comparative account of degradation efficiencies of our catalyst and various other catalysts reported in literature [20,29]. The reaction conditions and light source are not identical for the present and reported works and hence they are also given in Table 6.7. A rational comparison of all these data yields that our catalyst has better performance.
Table 6.7. Comparative account of degradation efficiencies of present and reported catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Light source</th>
<th>Reaction condition</th>
<th>% of Degradation and time</th>
<th>Reference</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO₂/Zeo-NaX</td>
<td>100 W tungsten lamp</td>
<td>pH = 6.9, [BG] = 10 ppm, T = RT, H₂O₂ = 2ml</td>
<td>94.8% in 3 h</td>
<td>This work</td>
</tr>
<tr>
<td>CeO₂/MCM-41</td>
<td>70 W Hg lamp</td>
<td>pH = 7-8 [CR] = 10 mg/l, T = RT, catalyst- 0.7g/l</td>
<td>97.6% in 3h</td>
<td>[11]</td>
</tr>
<tr>
<td>CeO₂/MCM-48</td>
<td>70 W Hg lamp</td>
<td>pH = 7-8 [CR] = 10 mg/l, T = RT, catalyst- 0.7g/l</td>
<td>93.1% in 3h</td>
<td>[11]</td>
</tr>
<tr>
<td>CeO₂/SiO₂</td>
<td>150 W Hg lamp</td>
<td>pH = 7-8 [MB] = 10 ppm, T = RT, catalyst = 0.4g/l</td>
<td>99.9 % in 1 h</td>
<td>[20]</td>
</tr>
</tbody>
</table>

CR- Congo red

6.4. Conclusions

Zeo-NaX prepared from waste coal fly ash and incorporated with nano cerium oxide has a considerable level of photocatalytic activity for brilliant green dye degradation. In view of environmental and economic aspects, production of fly ash converted Zeo-NaX from fly ash may provide cost-effectiveness to commercial zeolites. Hence, the novel catalyst has many potential applications because of its good structural stability, simple preparation, and stable catalytic activity in a repetitive reaction cycle and reusability. The results show that the catalyst is effective only for cationic dyes BG and MB and not for anionic MO/neutral p-NA molecule photodegradation.
6.5. References

