Ce$_{1-x}$Fe$_x$O$_2$ nanocatalysts for priority organic pollutants removal through catalytic wet air oxidation

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Abstract

A series of Ce$_{1-x}$Fe$_x$O$_2$ nanocatalysts, prepared by co-precipitation method, were applied for the catalytic oxidation of priority organic pollutants present in paper industry wastewater. To investigate the synergic effect of various Fe contents, detailed characterizations of Ce$_{1-x}$Fe$_x$O$_2$ were done by Raman, XPS, XRD, TEM and EDX techniques. The addition of Fe to CeO$_2$ lattice increased the amount of oxygen vacancies, which have an efficient role in the oxidation of organic pollutants under oxygen-rich conditions. Ce$_{0.4}$Fe$_{0.6}$O$_2$ catalyst showed the highest removal of TOC (72%), AOX (68%), chlorophenols (62%) and chloroguaicols (86%). The superior catalytic activity of Ce$_{0.4}$Fe$_{0.6}$O$_2$ is ascribed to its higher oxygen vacancy concentration. The presence of two oxidation states of Ce (4$+$/3$+$) and Fe (3$+$/2$+$) confirmed the role of redox couples in oxidation of organic pollutants.

Keywords: Ce$_{1-x}$Fe$_x$O$_2$, nanocatalyst, oxygen vacancy, wet air oxidation, chlorophenolics

I. Introduction

Today, the water pollution has become a global menace. The discharge of untreated industrial wastewaters is the main cause behind water pollution [1]. The increasing fresh water demand and stringent regulations have forced the industry to adopt the treatment techniques prior to discharge of wastewater to the environment. Biological methods have been widely explored, but the presence of non-biodegradable and toxic compounds in industrial wastewaters limits their application [2]. Catalytic wet air oxidation (CWAO) has a lot of potential towards the oxidation of organic compounds present in industrial wastewaters. High operating temperature and pressure limit the application of CWAO, confronted with the special equipment [3,4]. The development of catalyst with high activity is still a challenging task [5]. Metal oxides are important class of catalysts and they are widely reported to serve as a substitute to the noble metals for various catalytic reactions. Recently, CeO$_2$ has attracted considerable interest as an environmental catalyst. The activity of CeO$_2$ is due to its oxygen vacancy defects and high oxygen storage capacity associated with the facile transformation between Ce$^{4+}$ and Ce$^{3+}$ [6]. However, poor thermal stability of the pure CeO$_2$ is disadvantageous for catalysis. The mixed metal oxides (MMOs) of CeO$_2$ with various transition metals have demonstrated the better oxygen storage capacity and catalytic properties than the pure CeO$_2$ [7,8]. In general, the activity of a catalyst is associated with various structural factors, like chemical composition, specific surface area and surface oxygen vacancies [9]. The nanomaterials are reported to exhibit the high activity and stability in catalytic reactions, mainly due to their high specific surface area and better dispersion of active components. Therefore, nanocrystalline ceria-transition metal MMOs can be thought as an efficient heterogeneous catalyst for CWAO. Here Fe was selected for the formation of MMOs with CeO$_2$, as Fe-based materials are particularly appealing in the field of catalysis [10–12].

In this study, the Ce$_{1-x}$Fe$_x$O$_2$ nanocatalysts were investigated for catalytic wet air oxidation of paper industry wastewater through CWAO. The relationship between structural properties and oxidation behaviours of Ce$_{1-x}$Fe$_x$O$_2$ mixed oxides was established by different characterization techniques.
II. Material and methods

2.1. Wastewater sample

The wastewater sample was collected from primary clarifier outlet of a paper industry. The paper industry wastewater is highly polluted and characterized by high total organic carbon (TOC). The chlorinated compounds generated during bleaching are in particular the most harmful toxicants. Various chlorinated organic compounds identified in paper industry wastewater include chlorinated hydrocarbons, chloroform, furans, dioxins, chlorophenols etc. [13,14]. These chlorinated compounds are collectively estimated as adsorbable organic halides (AOX). Out of these, chlorophenolic compounds and their derivatives are major environmental concern, due to their persistence and adverse effects including carcinogenicity, dermal adsorption paralysis, injurious effects on reproductive and haematological organs of humans and the ecosbiota [15,16]. Some of these compounds have been classified as priority pollutants by EPA, US [17]. The chlorophenols (CP) and chloroguaiacs (CG) are quantitatively significant chlorophenolic compounds in paper industry wastewater [18].

2.2. Catalyst synthesis and characterization

The Ce$_{1-x}$Fe$_x$O$_3$ nanocatalysts with different Fe content ($x = 0.2, 0.4, 0.6, 0.8$) were prepared by co-precipitation method [19]. The pure CeO$_2$ and Fe$_2$O$_3$ catalysts were also synthesized. The catalysts were characterized by XRD, TEM, EDX, Raman and XPS techniques. The XRD pattern were recorded on Bruker AXS D8 X-ray diffractometer equipped with CuKα radiation ($\lambda = 0.154\text{nm}$). TEM analysis was carried out on Tecnai G$^2$ STWIN microscope operating at an accelerating voltage of 200kV. The EDX analysis was done by Oxford Instruments, 51 XMX 1005. Raman analysis was performed on Invia Renishaw spectrometer at 514 nm excitation line of Ar ion laser. The XPS spectra were obtained by PHI 5000 Versa Probe instrument.

2.3. Analytical methods

The TOC value of the wastewater sample was measured by Shimadzu TOC-L CPH analyser, where the difference between total carbon (TC) and total inorganic carbon (IC) gave the TOC value. AOX value was analysed by a Dextar AOX analyser based on combustion ion chromatography. The chlorophenolic compounds (CHPs) were quantified by GC-MS (Trace GC Ultra-DSQ, Thermo Electron Corporation) equipped with a TR-5 capillary column. CHPs were first extracted from the wastewater by liquid-liquid extraction method and then derivatized by acetic anhydride. The quantitative analysis of CHPs was carried out with the help of calibration curve of standard compounds.

III. Results and discussion

3.1. Structural characterization

Figure 1 presents the XRD pattern of CeO$_2$, Fe$_2$O$_3$ and Ce$_{1-x}$Fe$_x$O$_3$ nanocatalysts. The diffraction pattern for CeO$_2$ matches well with the characteristic cubic phase (JCPDS 81-0792). Fe$_2$O$_3$ presented the characteristic reflections of tetragonal hematite structure (JCPDS 86-0550). For Ce$_{1-x}$Fe$_x$O$_3$ nanocatalysts, the peaks corresponding to Fe$_2$O$_3$ phase appeared in the sample with 80 at.% Fe, indicating the solid solubility of Fe$_2$O$_3$ into CeO$_2$ up to 60 at.% [19]. For Ce$_{1-x}$Fe$_x$O$_3$ nanocatalysts, the characteristic ceria peaks were shifted towards higher values indicating the lattice deformation due to the presence of oxygen vacancies.

Raman spectroscopy was carried out to characterize the oxygen vacancies within catalysts. Raman spectra of Ce$_{1-x}$Fe$_x$O$_3$ nanocatalysts are presented in Fig. 2. CeO$_2$ exhibited a prominent Fe$_2$O$_3$ peak at 460 cm$^{-1}$, corresponding to the symmetric breathing mode of oxygen atoms around cerium ions (Ce$^{4+}$) [20]. For Ce$_{1-x}$Fe$_x$O$_3$ nanocatalysts, a less-prominent broad band was observed in the range from 530 to 740 cm$^{-1}$. This
broad band was deconvoluted into two bands centred at 600 cm⁻¹ and 675 cm⁻¹, respectively. The first band at 600 cm⁻¹ was related to the intrinsic oxygen vacancies which are formed due to the presence of Ce⁴⁺ [21]. In particular, this band was attributed to the Raman intensities which are formed due to the presence of Ce⁴⁺ at 600 cm⁻¹. The second weak band at 675 cm⁻¹ was attributed to the Raman intensity caused by relaxation of symmetry selection rules. The second weak band at 675 cm⁻¹ indicated the presence of small amount of Fe₂O₃ in the surface layer of nanocatalysts [22]. The shifting of Raman peaks towards lower wavenumber indicates the increase in oxygen vacancies, which is related to the structural defects derived from the incorporation of Fe into CeO₂ lattice. The concentration of oxygen vacancies for all samples was compared by calculating the intensity ratio I₆₀₀/I₄₆₀ of bands at 600 and 460 cm⁻¹. Figure 3 shows the variation of I₆₀₀/I₄₆₀ as a function of Fe concentration. The intensity ratio I₆₀₀/I₄₆₀ increased with increasing Fe content and reached a maximum for Ce₀.₄Fe₀.₆O₂ mixed oxide. The value of I₆₀₀/I₄₆₀ was high [23,24] and indicates the appreciably high concentration of oxygen vacancies. Fe₂O₃ exhibited the Raman peaks at 225, 245, 292, 408 and 497 cm⁻¹, corresponding to α-Fe₂O₃ [25].

The oxidation state of metal ions in Ce₀.₄Fe₀.₆O₂ nanocatalysts was confirmed by XPS analysis. Ce 3d spectra (Fig. 4a) exhibited the three main 3d₃/₂ features at the binding energies of 881.8, 887.6 and 897.4 eV corresponding to v, v', v'' components, respectively. The 3d₅/₂ feature corresponding to u, u' and u'' components were observed at 899.9, 906.1 and 915.7 eV. The v, v', v'', u, u' and u'' peaks with v and u splitting of 18.4 eV are the characteristic of Ce⁴⁺ oxidation state (CeO₂). Additional peaks corresponding to v' (884 eV), u' (902 eV), v'' (880.8 eV) and u'' (899 eV) components indicated the presence of Ce⁴⁺. The XPS results suggest that there is a certain amount of Ce⁴⁺ [26]. The atomic fraction of Ce⁴⁺ calculated from the integrated peak areas was found to be 28 at.%. This percentage indicates the presence of the significant number of oxygen vacancies [27,28]. Figure 4b presents the Fe 2p core level binding energy spectra for Ce₀.₄Fe₀.₆O₂ nanocatalyst. After refined fitting, the spectrum was deconvoluted into four peaks with strong binding energies centred at around 709.4 and 723 eV assigned to Fe²⁺. The peaks centred at about 711.5 and 725 eV can be ascribed to the presence of Fe⁴⁺. The spectra also exhibited well-defined shake-up satellite peaks at 716.8 eV and 731.7 eV [29,30]. These results suggest the coexistence of Fe²⁺/Fe⁴⁺ ion couple in Ce₁₋ₓFeₓO₂ nanocatalysts. O 1s spectra (Fig. 4c) exhibited three components, the relative percentage of each component is provided in parenthesis. The peak centred at 528.5 eV was related to the lattice oxygen (69.5%). The peak at 531.4 eV indicated the presence of adsorbed surface oxygen in the form of OH⁻ ions (9.4%). The additional peak at 530.2 eV was related to the supercharged oxygen (O⁻) near the oxygen vacant sites at the surface (21%) [31]. These results suggest that the Ce₁₋ₓFeₓO₂ nanocatalysts have better oxygen storage capacity, which would be advantageous for their higher catalytic oxidation activity.

Thus, Raman and XPS results revealed that the oxygen vacancies were generated by the incorporation of Fe ion into the ceria lattice to compensate the valence mismatch between the Fe²⁺/Fe⁴⁺ and Ce⁴⁺/Ce⁴⁺ ions. These results also provide evidence for the existence of redox equilibrium of Fe⁴⁺ + Ce⁴⁺ → Fe²⁺ + Ce⁶⁺, which is the source of a synergistic interaction between iron and ceria species in the Ce₁₋ₓFeₓO₂ nanocatalysts.

The morphology and microstructure of nanocatalysts...
were studied by TEM analysis. TEM micrographs of samples are shown in Fig. 5, and the particle sizes measured from micrographs are given in Table 1. The micrographs clearly illustrate that all the samples are aggregated nanoparticles with non-uniform pores. The average particle size of CeO$_2$ was 11 nm, where most of the particles were spherical and some were elongated in shape. For Ce$_{1-x}$Fe$_x$O$_2$ MMOs, the particles are nearly uniform spheres with diameters in the range of 8 to 5 nm. The decrease in particle size with addition of Fe can be related to the inhibition of growth of nanocrystals in presence of Fe ions [32]. Fe$_2$O$_3$ particles are also near uniform spheres but slightly larger than those of Ce$_{1-x}$Fe$_x$O$_2$ MMOs.

The elemental mapping results illustrate that the samples are MMOs. The quantitative EDX analysis confirmed that the actual Ce/Fe mole ratio in the catalysts was close to the expected values (Table 1).

### Table 1. Crystallite size (from XRD), particle size (from TEM) and elemental analysis (EDS) of catalysts

<table>
<thead>
<tr>
<th>Sample</th>
<th>Crystallite size [nm]</th>
<th>Particle size [nm]</th>
<th>Ce/Fe molar ratio</th>
<th>Expected</th>
<th>Obtained</th>
</tr>
</thead>
<tbody>
<tr>
<td>CeO$_2$</td>
<td>24</td>
<td>19 ± 2</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Fe$</em>{0.2}$O$_2$</td>
<td>8.7</td>
<td>8.9 ± 0.3</td>
<td>4</td>
<td>4.1</td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.8}$Fe$</em>{0.4}$O$_2$</td>
<td>8.9</td>
<td>8.2 ± 0.2</td>
<td>1.5</td>
<td>1.6</td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.6}$Fe$</em>{0.4}$O$_2$</td>
<td>8.2</td>
<td>7.8 ± 0.5</td>
<td>0.66</td>
<td>0.63</td>
<td></td>
</tr>
<tr>
<td>Ce$<em>{0.2}$Fe$</em>{0.8}$O$_2$</td>
<td>5.3</td>
<td>5.1 ± 0.2</td>
<td>0.25</td>
<td>0.25</td>
<td></td>
</tr>
<tr>
<td>Fe$_2$O$_3$</td>
<td>11</td>
<td>9.8 ± 0.4</td>
<td>–</td>
<td>–</td>
<td>–</td>
</tr>
</tbody>
</table>

### 3.2. Catalyst activity

The paper industry wastewater presented high organic load in terms of TOC (172 mg/l), AOX (16.2 mg/l), CPs (275 µg/l) and CGUs (193 µg/l) [33]. To investigate the catalytic properties of Ce$_{1-x}$Fe$_x$O$_2$ nanocatalysts, their catalytic wet air oxidation activity (CWAO) was explored. The CWAO of the wastewater sample was carried out under oxygen-rich conditions in a glass reactor at atmospheric pressure, catalyst dose 1 g/l, pH ~4, temperature 90 °C and reaction time 2 h [19]. Aliquots were taken out after treatment and the catalyst was separated by centrifugation. For comparison, the CWAO activity of the pure CeO$_2$ and Fe$_2$O$_3$ was also investigated under the same conditions.

### TOC and AOX removal

Figure 6 presents the abatement of TOC and AOX by CWAO using CeO$_2$, Ce$_{0.8}$Fe$_{0.2}$O$_2$, Ce$_{0.6}$Fe$_{0.4}$O$_2$, and Fe$_2$O$_3$. 
Ce\textsubscript{0.4}Fe\textsubscript{0.6}O\textsubscript{2}, Ce\textsubscript{0.2}Fe\textsubscript{0.8}O\textsubscript{2} and Fe\textsubscript{2}O\textsubscript{3}, CeO\textsubscript{2} was found to be the least active catalyst with 24% TOC and 21% AOX abatement. Fe\textsubscript{2}O\textsubscript{3} catalyst also exhibited the low abatement profile with 42% TOC and 38% AOX abatement. All the mixed catalysts exhibited higher removal efficiency, which increased with increasing Fe content and reached the maximum with Ce/Fe mole ratio of 40/60 (72% TOC and 68% AOX). The results show that the incorporation of Fe in CeO\textsubscript{2} can promote the catalytic activity, which could be interpreted in terms of synergistic interaction between iron and ceria species in Ce\textsubscript{1-x}Fe\textsubscript{x}O\textsubscript{2} nanocatalysts.

The highest efficiency of Ce\textsubscript{0.4}Fe\textsubscript{0.6}O\textsubscript{2} can be ascribed to the high oxygen vacancy concentration, as indicated by Raman analysis. On the basis of Raman and XPS results it can be concluded that Ce\textsuperscript{4+} and Fe\textsuperscript{3+} are easily reducible to Ce\textsuperscript{3+} and Fe\textsuperscript{2+}, respectively. These Ce\textsuperscript{3+} and Fe\textsuperscript{2+} ions are the active sites, where the reactant molecule is oxidized by the interface lattice oxygen, generating the oxygen vacancy. The oxygen vacancy is filled up by the gaseous O\textsubscript{2}, forming adsorbed active oxygen species which can react with another reactant molecule. Thus, the oxygen vacancies lead to the high oxygen mobility which is the main factors influencing the activity of catalytic oxidation.

**Chlorophenols (CPs) removal**

GC-MS analysis of chlorophenolics revealed the presence of total 13 chlorophenols (CPs) in the paper industry wastewater. The contribution from monochlorophenols (MCPs), di-chlorophenols (DCPs), tri-chlorophenols (TCPs) and penta-chlorophenols (PCPs) was 7.7%, 41%, 51% and 0.14%, respectively (Fig. 7a). Total amount of chlorophenols was 275 µg/l with major share of 2,4,5-TCP (132.9 µg/l), 2.5-DCP (62.4 µg/l), 2.4-DCP (26.5 µg/l) and 2.6-DCP (22.9 µg/l), while the rest of CPs were present in relatively lower quantities. Based on TOC and AOX removal efficiency, the Ce\textsubscript{0.4}Fe\textsubscript{0.6}O\textsubscript{2} mixed oxide was selected for the CWAO of chlorophenolics. After CWAO, a noticeable removal of CPs (62%) was achieved. The removal of individual CPs is given in Table 2. Results indicate that the removal of most of CPs was from 50% to 100%. PCP was completely removed or its concentration fallen below the detection limit of instrument. 3,4-DPC was removed up to 96%, followed by 2,3,4-TCP (87%), 2,3,5-DPC (87%), 2,4,6-TCP (86%), 2,6-DCP (72%), 2,4,5-TCP (63%), 2,4-DCP (59%), 4-CP (59%), 2.5-DCP (58%) and 3-CP (50%). The rest of the compounds was removed up to 24–26% only. Based on Cl substitution, the removal of PCPs, TCPs, DCPs and MCPs was 100%, 62%, 62% and 53%, respectively (Fig. 7b).

**Chloroguaicols (CGUs) removal**

A total amount of 193 µg/l of chloroguaicols (CGUs) was detected in paper industry wastewater, with major share from 4,5-DGU (103 µg/l) and 4-CGU (84 µg/l), while the rest of CGUs was present in relatively very low quantity. The di-chloroguaicols (DGCUs), mono-chloroguaicols (MCGUs), tri-chloroguaicols (TCGUs) and tetra-chloroguaicols (TeCGUs) comprised 55%, 43%, 0.97% and 0.94% of the total amount of CGUs (Fig. 8a).

After CWAO 86% removal of CGUs was observed. The removal of each individual CGU is presented in Table 3. The results indicate that the removal of most of CGUs was from 81% to 100%. Maximum removal efficiency was achieved for 4,5-DGU (89%), followed
Figure 8. Chloroguaicols: a) initial concentration before CWAO and b) concentration after CWAO

Table 3. Concentration of chloroguaicols in paper industry wastewater before and after CWAO

<table>
<thead>
<tr>
<th>Compound</th>
<th>Before CWAO [µg/l]</th>
<th>After CWAO [µg/l]</th>
<th>[%] removal</th>
</tr>
</thead>
<tbody>
<tr>
<td>4-CG</td>
<td>83.6 ± 19.5</td>
<td>13.3 ± 1.2</td>
<td>84</td>
</tr>
<tr>
<td>4,5-DCG</td>
<td>103 ± 1.9</td>
<td>11.6 ± 1.9</td>
<td>89</td>
</tr>
<tr>
<td>4,6-DCG</td>
<td>2.6 ± 0.5</td>
<td>1.2 ± 0.04</td>
<td>89</td>
</tr>
<tr>
<td>3,4,5-TCG</td>
<td>0.6 ± 0.1</td>
<td>0.4 ± 0.4</td>
<td>33</td>
</tr>
<tr>
<td>3,4,6-TCG</td>
<td>0.5 ± 0.2</td>
<td>ND</td>
<td>81</td>
</tr>
<tr>
<td>4,5,6-TCG</td>
<td>0.7 ± 0.1</td>
<td>0.1 ± 0.02</td>
<td>81</td>
</tr>
<tr>
<td>Tet-CG</td>
<td>1.8 ± 0.2</td>
<td>0.3 ± 0.05</td>
<td>86</td>
</tr>
<tr>
<td>Total</td>
<td>193</td>
<td>27</td>
<td>86</td>
</tr>
</tbody>
</table>

by Tet-CGU (86%), 4-CGU (84%), 4,5,6-TCGU (81%) and 4,6-DCGU (56%). Minimum removal of 33% was obtained for 3,4,5-TCGU. Based on Cl atom substitution, the degradation of TeCGUs, TCGUs, DCGUs and MCGUs was 85%, 77%, 89% and 84%, respectively (Fig. 8b).

Various CWAO studies have been reported in presence of ceria based catalysts. Ru/Ce$_{1-x}$Zr$_x$O$_2$ catalyst exhibited up to 43% TOC abatement from surface plating industry wastewater at 150°C and 0.6 MPa [34]. Ag/Ce$_{0.85}$Zr$_{0.15}$O$_2$ catalyst achieved 76% removal of bisphenol A at 160°C and 2 MPa [35]. CeO$_2$-TiO$_2$ catalyst showed 100% COD and 77% TOC removal of phenol at 150°C and 3 MPa [36]. In this line, our result indicates the suitability of Ce$_{1-x}$Fe$_x$O$_2$ nanocatalysts for removal of TOC, AOX, chlorophenols and chloroguaicols at mild operating conditions.

### 3.3. Kinetic studies

The time dependent TOC removal was studied in order to understand the rate of reaction during oxidation. The experimental data obtained with time-dependent TOC removal in presence of Ce$_{0.4}$Fe$_{0.6}$O$_2$ catalyst was modelled on the assumption of first-order kinetics, as follows [37]:

\[
-\frac{d[TOC]}{dt} = k_1 \cdot [TOC]
\]

By integrating Eq. (1):

\[
\int_0^{[TOC]_0} \frac{d[TOC]}{[TOC]} = k_1 \cdot \int_0^t dt
\]

the following relation can be obtained:

\[
\ln \left(\frac{[TOC]_0}{[TOC]}\right) = k_1 \cdot t
\]

The experimental data fitted well for the first order kinetics, as straight line with $R^2$ value of 0.96 was obtained in the plot constructed between $\ln([TOC]_0/[TOC])$ and time (t) (Fig. 9). Thus the CWAO of wastewater in presence of Ce$_{1-x}$Fe$_x$O$_2$ nanocatalysts was found to follow the first order kinetics.

Figure 9. Plot of $\ln([TOC]_0/[TOC])$ as a function of reaction time

### IV. Conclusions

Ce$_{1-x}$Fe$_x$O$_2$ nanocatalysts were synthesized by co-precipitation method. The characteristics of nanocatalysts with different Fe contents were studied by various techniques. The activity of nanocatalysts was explored for the catalytic wet air oxidation of industrial wastewater. The Ce$_{0.4}$Fe$_{0.6}$O$_2$ nanocatalyst presented the appreciable removal of TOC, AOX, chlorophenols and chloroguaicols. The characterization results revealed that the presence of Ce$^{3+}$ and Fe$^{2+}$ and richer surface oxygen vacancies are responsible for the better performance of Ce$_{1-x}$Fe$_x$O$_2$ nanocatalysts. The results provide an efficient catalyst for removal of priority organic pollutants from the complex industrial wastewater through the catalytic wet air oxidation.

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