Heterogeneous Fenton-like oxidation of p-hydroxybenzoic acid using Fe/CeO₂-TiO₂ catalyst

Tijani Hammedi, Mohamed Triki, Mayra G. Alvarez, Jordi Llorca, Abdelhamid Ghorbel, Zouhaier Ksibi and Francesc Medina

ABSTRACT

This paper is built on the Fenton-like oxidation of p-hydroxybenzoic acid (p–HBZ) in the presence of H₂O₂ and 3%Fe supported on CeO₂-TiO₂ aerogels under mild conditions. These catalysts were deeply characterized by X-ray diffraction (XRD), hydrogen temperature programmed reduction (H₂-TPR), transmission electron microscopy (TEM), scanning transmission electron microscopy (STEM) and X-ray photoelectron spectroscopy (XPS). The effect of thermal treatment, pH (2–3, 5, 7), H₂O₂/p–HBZ molar ratio (5, 15, 20, 25) and reaction temperature (25 °C, 40 °C and 60 °C) on the catalytic properties of supported Fe catalysts are studied. Our results highlight the role of CeO₂ and the calcination of the catalyst to obtain the highest catalytic properties after 10 min: 73% of p–HBZ conversion and 52% of total organic carbon (TOC) abatement.

Key words | CeO₂, Fe catalyst, Fenton-like oxidation, p-hydroxybenzoic acid

INTRODUCTION

Advanced oxidation processes (AOPs) have been successfully used for the treatment of wastewaters to reduce the concentration of toxic organic pollutants. This technology is based on the in situ generation of hydroxyl radicals (HO·), which are highly reactive and non-selective. Wet hydrogen peroxide oxidation is one of the AOPs technologies, which is known to be efficient for the degradation of organic pollutants using hydrogen peroxide as the liquid oxidant (Kurian & Nair 2015; Hu & Long 2016). Since this process requires severe operation conditions and costly investment, many efforts have been made to use it at milder conditions via an appropriate catalyst. In this context, heterogeneous Fenton-like reaction based on nanomaterials at mild conditions has gained attention as one of the most important catalytic processes for the oxidation of dissolved organic pollutants (Hartmann et al. 2010; Bokare & Choi 2014; Pouran et al. 2014; Munoz et al. 2015). Recently, several heterogeneous catalysts have been studied in Fenton-like oxidation of different organic contaminants such as magnetite/Fe-Al-montmorillonite (Wei et al. 2017), CuFe-carbon (Wang et al. 2015), Iron-alumina (Di Luca et al. 2015), Ag/CeO₂ (Aneaggi et al. 2017), CeO₂–H₂O₂
system with Fe$^{3+}$ doping (Cai et al. 2010), S-doped α-Fe$_2$O$_3$ (Guo et al. 2010), α-Fe$_2$O$_3$/Bi$_2$O$_3$Cl$_2$ (Chang et al. 2018), and α-Fe$_2$O$_3$/graphene oxide (Liu et al. 2017). Moreover, CeO$_2$ is able to activate H$_2$O$_2$ by a Fenton-like reaction due to the availability of Ce$^{3+}$ oxygen vacancies on the oxide surface (Mamontov et al. 2000). In addition to that, the oxidation-reduction process of the Ce species occurs more easily on the surface of the particle (Ce$^{4+}$/Ce$^{3+}$ cycle), producing an easy formation and elimination of oxygen defects during catalytic applications (Campbell & Peden 2005). The use of CeO$_2$ as heterogeneous Fenton-like catalyst by generating HO$^-$ radicals was proved in the presence of H$_2$O$_2$ (Heckert et al. 2008) as shown by the following reactions:

\[
\begin{align*}
\text{Ce}^{3+} + \text{H}_2\text{O}_2 + \text{H}^+ \rightarrow \text{Ce}^{4+} + \text{HO}^+ + \text{H}_2\text{O} & \quad (1) \\
\text{HO}^+ + \text{H}_2\text{O}_2 \rightarrow \text{HO}_2^- + \text{H}_2\text{O} & \quad (2) \\
\text{Ce}^{4+} + \text{HO}_2^- \rightarrow \text{Ce}^{3+} + \text{O}_2 + \text{H}^+ & \quad (3)
\end{align*}
\]

As mentioned in previous studies, the HO$^-$ production depends critically on the oxide surface properties (Ji et al. 2010). Without surface modification, the reaction between Ce$^{3+}$ and H$_2$O$_2$ leads to the formation of stable brown peroxide-like species (Ce$^{3+}$–OOH$^-$), which remain stable even at neutral pH and do not directly decompose to generate free HO$^-$ (Chen et al. 2012). The peroxide species are relatively chemically stable in the absence of organic contaminants and can only degrade substances absorbed on the surface of CeO$_2$ via an intermolecular rearrangement. As shown in Figure 1 the degradation of organics is a localized surface reaction rather than a radical-attack Fenton reaction in the CeO$_2$/H$_2$O$_2$ system (Wang et al. 2014).

Thus, the heterogeneous redox system CeO$_2$-H$_2$O$_2$ can be easily manipulated by simple surface modification to efficiently generate HO$^-$ under mild acidic conditions. The use of CeO$_2$ further amplifies the effective surface concentration of Ce$^{3+}$ and increases the overall HO$^-$ yield, due to the critical role of surface Ce$^{3+}$ species on the catalytic efficiency. In our previous work, we found that CeO$_2$, when associated with TiO$_2$, promotes oxygen storage and enhances oxygen mobility, producing surface and bulk vacancies that improve the redox properties of the catalytic system (Hammadi et al. 2015a). However, CeO$_2$-TiO$_2$ mixed oxides have not been investigated yet as supports for catalysts in Fenton-like oxidation.

In this work, we explored the efficiency of the 3% Fe/CeO$_2$-TiO$_2$ catalysts for the Fenton-like oxidation of p-hydroxybenzoic acid (p–HBZ) in the presence of H$_2$O$_2$ at mild conditions. This molecule was chosen as a non-biodegradable model of phenolic pollutants typically found in olive oil mill wastewaters. We thoroughly studied the effect of pH, H$_2$O$_2$ concentration and reaction temperature on the catalytic properties of supported Fe catalysts. The CeO$_2$-TiO$_2$ mixed oxides as well as the Fe catalysts were deeply characterized by XRD, H$_2$-TPR, TEM, STEM and XPS.

### EXPERIMENTAL

#### Catalysts preparation

CeTi and TiO$_2$ were prepared via the sol-gel method as described previously (Hammadi et al. 2015a). CeTi was prepared by dissolving Cerium(III) nitrate hexahydrate in anhydrous ethanol in the presence of ethyl acetoacetate. Titanium(IV) isopropoxide was then added to the mixture in different molar ratios of Ce/Ti: 1/4, 1/5 and 1/6. Homogeneous gels, obtained after addition of HNO$_3$ (0.1 mol/L), were transferred to an autoclave for a supercritical drying at T = 243 °C and P = 64 bars. All samples were calcined under oxygen at 500 °C for 3 h. TiO$_2$ was prepared by the same described protocol without the addition of the cerium salt. The Fe (3 wt%) catalysts were prepared by incipient wetness impregnation of the support with an aqueous solution of Fe(NO$_3$)$_3$·9H$_2$O. The obtained solids were dried overnight at 90 °C for 24 h and then calcined under O$_2$ at 300 °C for 2 h. The samples were named as 3Fe/Ti–C and 3Fe/CeTi–C. Some samples were reduced under H$_2$ for 2 h at 500 °C and labelled as 3Fe/CeTi–R. The Ce/Ti molar ratio chosen for the preparation of the 3Fe/CeTi catalysts is 1/5. Particularly, the chemical composition of 3Fe/CeTi–C was checked by SEM-EDX.

![Figure 1](http://www.iwaponline.com/wst/article-pdf/79/7/1276/618590/wst079071276.pdf)

**Figure 1 |** Equation of the decomposition of organics in the CeO$_2$/H$_2$O$_2$ system.
Catalysts characterization

N₂ physisorption studies were carried out in automatic Micromeritics ASAP 2020 apparatus. The specific surface area was determined using the Brunauer-Emmett-Teller (BET) method and the average pore size was calculated with the Barrett-Joyner-Halenda (BJH) method using isothermal desorption data. X-ray diffraction (XRD) measurements were performed using a Philips PW1050 diffractometer. The average crystallite size of the samples was estimated using the Debye-Scherrer equation. Hydrogen diffractometer. The average crystallite size of the samples measurements were performed using a Philips PW1050

\[ \text{FeI Tecnai G2 F20 S-TWIN field-emission gun transmission electron microscope (STEM) and energy dispersive X-ray analysis (EDX) were carried out with a FEI Tecnai G² F20 S-TWIN field-emission gun transmission electron microscope at 200 kV. X-ray photoelectron spectroscopy (XPS) was performed on a SPECS system equipped with an Al anode XR50 source operating at 150 mW and a Phoibos MCD-9 detector. The pass energy of the hemispherical analyzer was set at 25 eV and the energy step was set at 0.1 eV. The pressure in the analysis chamber was kept below } 10^{-7} \text{ Pa.} \]

Catalytic oxidation experiments

Catalytic tests were performed in a glass reactor at atmospheric pressure using 100 mL of p-HBZ aqueous solution (10 mmol/L) over supported Fe catalyst (50 mg) at fixed pH and temperature between 25 °C and 60 °C. The desired pH (2, 3.2, 5 and 7) of the solution was adjusted using HCl (0.1 mmol/L) or NaOH (0.1 mmol/L). After stirring for 30 min in order to reach the p-HBZ adsorption equilibrium, a volume of \( \text{H}_2\text{O}_2 \) was added to the solution and the reaction started. It is important to note that samples were withdrawn to assess adsorption before the addition of \( \text{H}_2\text{O}_2 \). The \( \text{H}_2\text{O}_2/\text{p-HBZ} \) molar ratio of 14/1 corresponds to the stoichiometric quantity needed for the total oxidation of p-HBZ to \( \text{CO}_2 \) and \( \text{H}_2\text{O} \) according to the following reaction:

\[
\text{C}_7\text{H}_6\text{O}_3 + 14\text{H}_2\text{O}_2 \rightarrow 7\text{CO}_2 + 17\text{H}_2\text{O} \tag{4}
\]

Therefore, 0.123 mL of \( \text{H}_2\text{O}_2 \) (11 mol/L) was added into the reactor to obtain an \( \text{H}_2\text{O}_2/\text{p-HBZ} \) molar ratio of 14/1. Different \( \text{H}_2\text{O}_2/\text{p-HBZ} \) molar ratios (5, 15, 20 and 25) are studied. The concentrations of p-HBZ and intermediates were monitored by high performance liquid chromatography (HPLC, Waters 1515) at \( \lambda = 254 \text{ nm} \) using a Hypersil Gold C18 column and acetonitrile/H₂O/Na₂SO₄ (0.005 mol/L) (20/70/10) as the mobile phase. Total organic carbon (TOC) was measured with a Shimadzu Model 5050 TOC analyzer. The initial reaction rate was calculated from the curve \( C \) versus time, where \( C \) is the concentration of p-HBZ after oxidation. It corresponds to the slope of the linear part of the curve at low p-HBZ conversion (<10% of conversion).

RESULTS AND DISCUSSION

Catalysts characterization

Table 1 shows the textural and structural properties of the prepared materials. BET surface areas of the CeO₂-TiO₂ materials are higher than the area obtained for pure TiO₂. This result could be attributed to the inhibition of particle growth for the CeTi mixed oxides, which can be verified by TEM analysis. As the content of cerium increases, the \( S_{\text{BET}} \) of CeTi increases to 183 m²/g for a Ce/Ti ratio of 1/5. This result could be due to the modification of the hydrolysis-condensation reactions’ rates by the cerium nitrate (Lopez et al. 2004). However, a decrease in pore diameter is observed when adding Ce to TiO₂, which could be due to the higher bond length of Ce-O (2.345 Å) (Shoko et al. 2009) compared to the bond length of Ti-O (1.952 Å) (Brown & Shannon 1973). BET surface areas of the supported Fe catalysts are lower than those of bare CeTi. In fact, the \( S_{\text{BET}} \) of 3Fe/CeTi-C and 3Fe/CeTi-R are

<table>
<thead>
<tr>
<th>Materials</th>
<th>( S_{\text{BET}} ) (m²/g)</th>
<th>Pore diameter (nm)</th>
<th>TiO₂ crystalite size (nm)</th>
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</thead>
<tbody>
<tr>
<td>TiO₂</td>
<td>82</td>
<td>21.0</td>
<td>49</td>
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<tr>
<td>CeTi(1/4)</td>
<td>110</td>
<td>19.7</td>
<td>40</td>
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<tr>
<td>CeTi(1/5)</td>
<td>183</td>
<td>9.0</td>
<td>9.0</td>
</tr>
<tr>
<td>CeTi(1/6)</td>
<td>124</td>
<td>16.7</td>
<td>10</td>
</tr>
<tr>
<td>5Fe/Ti-C</td>
<td>76</td>
<td>8.8</td>
<td>83</td>
</tr>
<tr>
<td>3Fe/CeTi-C</td>
<td>133</td>
<td>11.4</td>
<td>40</td>
</tr>
<tr>
<td>3Fe/CeTi-R</td>
<td>142</td>
<td>10.7</td>
<td>24</td>
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</table>

*By XRD.
133 m²/g and 142 m²/g, respectively compared to 183 m²/g for the CeTi(1/5) support. This result could be attributed to a certain blockage of the porous structure of the support by Fe species.

Figure 2 shows the XRD patterns of TiO₂, CeTi, 3Fe/Ti–C and 3Fe/CeTi. For TiO₂, only peaks corresponding to the anatase phase were detected (JCPDS 83-2243). For CeO₂, peaks at 2θ = 28.6°, 33.1°, 47.5° and 56.3° attributed to cubic structure were observed (JCPDS 43-1002). For the CeTi mixed oxides, peaks corresponding to TiO₂ anatase become weaker and broader, while peaks corresponding to CeO₂ are weaker, compared to those of pure oxides. Moreover, the crystallite size of TiO₂ in CeTi decreases, which suggests that the Ce species inhibit the growth of anatase crystallites (Table 1). The appearance of the CeO₂ phase simultaneously with the decrease of TiO₂ particle size is consistent with BET surface area results. The XRD patterns of Fe/CeTi are similar to those of CeTi without any crystalline phase corresponding to iron oxide. It can be noticed that TiO₂ crystalline phase in the 3Fe/CeTi–R catalyst is lower than in the calcined one (3Fe/CeTi–C). This result indicates that the reduction of the catalyst could lead to the segregation of iron particles in the CeTi mixed oxides.

Figure 3 shows the H₂–TPR profiles of the samples. Pure CeO₂ (Figure 3(a)) exhibits a broad reduction peak at 550 °C, which could be attributed to the reduction of Ce⁴⁺ to Ce⁵⁺ on the surface (Dutta et al. 2006). For the CeTi support (Figure 3(b)), the H₂–TPR profile exhibits a broad reduction peak between 250 °C and 500 °C (maximum at 460 °C), which is shifted to lower reduction temperatures compared to pure ceria. Therefore, the reduction of CeO₂ in the mixed support is facilitated in comparison with pure CeO₂. A broad peak for 3Fe/CeTi–C (Figure 3(c)) is observed at 350 °C, probably due to the reduction of iron oxide in strong interaction with the support (Hammadi et al. 2015b). For 3Fe/CeTi–R, a reduction peak is observed at 305 °C (Figure 3(d)), where the amount of hydrogen consumed (607 μmol/g) is similar to that of the calcined sample (585 μmol/g), which suggests that during the reduction the iron oxide species strongly interact with the CeTi support. For the 3Fe/Ti–C sample (Figure 3(e)), two broad reduction peaks are observed at 150 and 650 °C. The first peak is due to the presence of iron with no interaction with the TiO₂ support, while the second peak is probably due to the iron in the crystalline structure of the TiO₂ support.

Figure 4 presents TEM images of TiO₂, CeTi, 3Fe/CeTi–R and 3Fe/CeTi–C. Slight aggregates of TiO₂ particles are observed (Figure 4(a)), although better dispersion is achieved by doping with CeO₂ (Figure 4(b)). This observation could explain the fact that the BET surface area of CeTi is higher than the area obtained for pure TiO₂. Since the Fe–Ce ions are inserted into the lattice of TiO₂, the particles in 3Fe/CeTi–C (Figure 4(c)) and 3Fe/CeTi–R (Figure 4(d)) are well dispersed. STEM images of 3Fe/CeTi–C show well-dispersed iron particles at high magnification with no large aggregates (Figure S1, Supplementary information, available with the online version of this paper). EDX analysis (inset in Figure S1a) shows a uniform distribution of iron particles of 1–2 nm. Moreover, the EDX analyses of 3Fe/CeTi–C match well with the expected chemical compositions as shown in Table S1 (Supplementary information, available online).

XPS spectra of 3Fe/CeTi–C are shown in Figure 5 and the surface atomic ratios Ce/Ti, Fe/Ti and Fe/(Ce + Ti) are
given in Table S2 (Supplementary information, available online). The surface atomic Ce/Ti decreased in the presence of the iron species, which shows that Ce probably interacts with Fe particles. The XPS spectrum of the Fe2p region taken on the surface of 3Fe/CeTi-C (Figure 5(a)) shows the presence of satellite lines, indicating the presence of oxidized Fe (Nasralla et al. 2013). The XPS spectrum of Ce3d for 3Fe/CeTi-C (Figure 5(b)) reveals the presence of both Ce(III) and Ce(IV). The CeTi sample contained 17.2% of reduced Ce(III), whereas 3Fe/CeTi-C contained 22.2% of Ce(III). This means that the transition metal promotes the reduction of CeO₂ on the surface, suggesting a strong contact between the metal nanoparticles and the support. Ce⁵⁺ induces the formation of oxygen vacancies in the material, which are essential for adsorption/dissociation of oxygen molecules during the oxidation. The XPS spectrum

Figure 3 | H₂-TPR profiles of (a) CeO₂, (b) CeTi(1/5), (c) 3Fe/CeTi-C, (d) 3Fe/CeTi-R, and (e) 3Fe/Ti-C.

Figure 4 | TEM images of (a) TiO₂, (b) CeTi(1/5), (c) 3Fe/CeTi-C, and (d) 3Fe/CeTi-R.
of Ti2p for 3Fe/CeTi–C (Figure 5(c)) indicates the presence of Ti4⁺ in the CeTi mixed oxides. The XPS binding energy of O1 s at 530.4 eV is assigned to lattice oxygen, while the peak at 532.8 eV is ascribed to surface hydroxyl species (Figure 5(d)).

**Catalytic results**

Blank experiments were carried out to evaluate the eventual contribution of the non-catalytic system in p–HBZ oxidation and H₂O₂ decomposition. The results show that, without catalyst, the oxidation of p–HBZ and the decomposition of H₂O₂ are negligible at 60 °C using a (H₂O₂/p–HBZ) molar ratio of 14/1. Moreover, the results show that the adsorption of p–HBZ on the solid remains below 5.0%. In order to fix the amount of catalyst, experiments were performed in the presence of 3Fe/CeTi–C (15 mg, 20 mg and 50 mg) at 60 °C. We chose to perform the reaction with 30 mg of catalyst to ensure that there are no mass transfer limitations as shown in Figure S2 (Supplementary information, available online). Table 2 regroups the initial reaction rates and the catalytic properties of supported Fe catalysts for the oxidation of p–HBZ at 60 °C. The results show that 3Fe/CeTi–C leads to 73% of p–HBZ conversion after 10 min, compared to 37% with 3Fe/Ti–C and 2.5% with 3Fe/CeTi–R. These results could be related to the fact that 3Fe/CeTi–C presents a high surface area, high content of oxygen vacancies and a high concentration of Ce³⁺, permitting enhancement of oxygen adsorption on the catalyst surface, and so increasing the catalytic activity. In addition, the

<table>
<thead>
<tr>
<th>Catalysts</th>
<th>Rₒ⁺ (mol/g·min⁻¹)</th>
<th>TOC abatement (%) after 1 h</th>
<th>p–HBZ conversion (%) after 10 min</th>
<th>Hydroquinone (%) at 10 min</th>
<th>Maleic acid (%) at 10 min</th>
</tr>
</thead>
<tbody>
<tr>
<td>3Fe/Ti–C</td>
<td>0.150</td>
<td>48</td>
<td>37</td>
<td>5.9</td>
<td>0.03</td>
</tr>
<tr>
<td>3Fe/CeTi–C</td>
<td>0.166</td>
<td>52</td>
<td>73</td>
<td>15.0</td>
<td>0.31</td>
</tr>
<tr>
<td>3Fe/CeTi–R</td>
<td>0.110</td>
<td>42</td>
<td>2.5</td>
<td>1.2</td>
<td>0.06</td>
</tr>
</tbody>
</table>

*Initial reaction rate.
initial reaction rates of the supported Fe catalysts are quite high. However, the calcined catalyst (3Fe/CeTi–C) is more active than 3Fe/CeTi–R since its initial reaction rate reaches 0.166 mmol/(g·min) compared to 0.11 mmol/(g·min) for the reduced catalyst. The low initial reaction rate showed by the reduced catalyst suggests an induction period needed for this catalyst (3Fe/CeTi–R). This period could be due to a reduced concentration of chemisorbed oxygen and/or weakly bonded oxygen species on the CeTi mixed oxides. Despite the similar TPR profiles for 3Fe/CeTi–C and 3Fe/CeTi–R, it seems reasonable that the reduction step provokes changes at the material surface, which is mirrored in the catalytic activity. This reduction removes the surface oxygen species, so a re-oxidation step is necessary before the Fenton reaction. Hydroquinone and maleic acid are identified as intermediates and the evolution of their concentrations during the oxidation of p–HBZ over 3Fe/Ti–C, 3Fe/CeTi–C and 3Fe/CeTi–R is shown in Figure 6. Hydroquinone is produced at higher concentration, while maleic acid is produced at a lower concentration. In the presence of 3Fe/Ti–C, the concentration of hydroquinone reaches 0.397 mmol/L after 10 min and then decreases after 20 min of reaction. However, the 3Fe/CeTi–C catalyst leads to the highest hydroquinone concentration (0.478 mmol/L) after 10 min, which then decreases rapidly.

Effect of pH

The effect of pH on p–HBZ oxidation over 3Fe/CeTi–C in the presence of H₂O₂ is shown in Figure 7. The results show that the catalytic properties are affected when pH increases. In fact, p–HBZ conversion is higher than 70%
after 10 min at pH 2–3, whereas it decreases to 12% and 1.0% at pH 5 and pH 7, respectively. This result could be related to a decrease of the oxidation potential of OH due to the increase of pH (Kwon et al. 1999). Moreover, some active iron species cannot exist at neutral pH and thus cannot establish an effective Fenton-like reaction. When pH decreases, a sufficient amount of H₂O₂ is available producing hydroxyl radicals due to the generation of carboxylic acids. However, when pH increases, precipitation of insoluble ferric hydroxides takes place and the decomposition of H₂O₂ becomes preponderant. Therefore, at high pH, hydrogen peroxide is decomposed into H₂O and O₂ due to the iron precipitate, which suppresses the OH generation. Due to this decomposition, fewer hydroxyl radicals are formed and so weaker oxidation efficiency is achieved (Sreeja & Sosamony 2016). It could be concluded that pH value affects the formation of OH and so the oxidation efficiency, which reaches the maximum at pH 2. In our previous work (Hammadi et al. 2015b), no Fe leaching with high extent was observed and the inductive coupled plasma analyses showed that the maximum of Fe concentration detected in the solution was 5.4 mg/L at pH 3.4 after 1 h of reaction. This represents a leaching of 6.0% of Fe in the solution, indicating reasonably good stability in acidic pH, and probably the amount of leached Fe at higher pH could be considered negligible. A small contribution due to homogeneous Fenton might occur. However, this amount of leached Fe do not probably have a great effect on the p–HBZ oxidation rate, since it was found that the catalytic activity is related to Fe concentrations of 10 times higher than those found in our solutions (Rivas et al. 2001). Moreover, it is important to take into account that Fe leaching has to be produced progressively, thus a low amount of Fe could be found in the first minutes of reaction. For this reason, a heterogeneous mechanism of p–HBZ is most probably expected to occur. On the other hand, CeO₂ seems to improve catalytic stability by strengthening the interaction between Fe and the CeTi mixed oxides as found by H₂-TPR, which may lead to low Fe leaching.

**Effect of H₂O₂/p–HBZ molar ratio**

The Fenton-like oxidation of p–HBZ is governed by the generation of OH radicals, produced directly from the reaction between H₂O₂ and the supported Fe catalyst. These radicals are immediately consumed just after their rapid formation. Moreover, the effect of H₂O₂ content over catalytic efficiency is relevant to the OH radicals amount. Therefore, the choice of an optimum H₂O₂/p–HBZ molar ratio is important to get the highest oxidation efficiency. Figure 8 shows the effect of H₂O₂ concentration on p–HBZ conversion and TOC abatement when p–HBZ oxidation was performed over 3Fe/CeTi–C at 60 °C. It can be noted that the conversion of p-HBZ is enhanced with the increase of the H₂O₂/p–HBZ molar ratio. A total conversion of p–HBZ is achieved after 20 min for H₂O₂/p–HBZ molar ratios of 15 and 20. This result could be attributed to the presence of more OH radicals on the surface of 3Fe/CeTi–C, which is in agreement with previous studies (Chang et al. 2018). However, when the H₂O₂/p–HBZ molar ratio is 25, the oxidation efficiency decreases to 78%. Therefore, the further increase in H₂O₂ concentration does not lead to a higher
oxidation rate, which could probably be due to a scavenging effect of \( \cdot \text{OH} \). In fact, \( \cdot \text{OH} \) is a powerful scavenger, which may react with \( \text{H}_2\text{O}_2 \) according to the following reactions:

\[
\begin{align*}
\text{H}_2\text{O}_2 + \cdot \text{OH} & \rightarrow \text{HO}_2^- + \text{H}_2\text{O} \\
\text{HO}_2^- + \cdot \text{OH} & \rightarrow \text{O}_2 + \text{H}_2\text{O}
\end{align*}
\]

The hydroperoxyl radical (\( \text{HO}_2^- \)) generated is less reactive than \( \cdot \text{OH} \) and does not contribute to the degradation of organic pollutants, which only occurs in the presence of \( \cdot \text{OH} \) radical (Shukla et al. 2010; Liu et al. 2017). Therefore, an appropriate molar ratio of \( \text{H}_2\text{O}_2/p\)-HBZ is required to avoid the excess of \( \text{H}_2\text{O}_2 \) and so the decrease of oxidation efficiency.

**Effect of reaction temperature**

The effect of reaction temperature on the catalytic behavior of \( 3\text{Fe}/\text{CeTi-C} \) is shown in Table 3. As expected, \( p\)-HBZ conversion and TOC abatement are enhanced when the temperature increases. In fact, \( p\)-HBZ conversion increases from 7.0% to 25% at 25 °C and 40 °C, respectively, and reaches 73% at 60 °C after 10 min of reaction. Moreover, the initial reaction rates increase from 0.02 mmol/(g·min) at 25 °C to 0.166 mmol/(g·min) at 60 °C. This result could be due to a higher rate of \( \text{H}_2\text{O}_2 \) conversion into \( \cdot \text{OH} \) at higher temperature leading to a smaller amount of \( \text{H}_2\text{O}_2 \) to scavenge these radicals (Inchaurreondo et al. 2012).

**Kinetic study**

To reveal the catalytic reaction kinetics, \( \ln(C_0/C_t) \) versus time at different temperatures are plotted as shown in Figure 9. The linear fit of \( \ln(C_0/C_t) \) versus time indicates that the oxidation of \( p\)-HBZ follows a pseudo-first order kinetic. Therefore, the following equation can be applied:

\[
\ln \left( \frac{C_0}{C_t} \right) = (k_{\text{app}}) \cdot t
\]

where \( C_0 \) and \( C_t \) are the concentrations of \( p\)-HBZ (mmol/L) at time 0 (min) and \( t \) (min), respectively, and \( k_{\text{app}} \) is the apparent reaction rate constant (min\(^{-1}\)).

It is obvious that the apparent reaction rate constant is improved with increasing the reaction temperature. Accordingly, the apparent reaction rate constants are 0.007 min\(^{-1}\), 0.029 min\(^{-1}\) and 0.125 min\(^{-1}\) at 25 °C, 40 °C and 60 °C, respectively. In fact, \( p\)-HBZ oxidation is faster at high temperature due to rapid activation of \( \text{H}_2\text{O}_2 \). It is important to note that the temperature should be below 80 °C to prevent the decomposition of \( \text{H}_2\text{O}_2 \) into \( \text{O}_2 \) and \( \text{H}_2\text{O} \). The activation energy \( (E_a) \) could be calculated according to the following Arrhenius equation:

\[
\ln k_{\text{app}} = \ln A - \frac{E_a}{RT}
\]

where \( A \) is the Arrhenius factor and \( k_{\text{app}} \) is the apparent reaction rate constant (min\(^{-1}\)).

The activation energy can be calculated from the slope of the \( \ln k_{\text{app}} \) versus \( 1/T \) linear curve (Figure S3, Supplementary Information, available online). The \( E_a \) value is determined as 67.8 ± 0.5 kJ/mol for the \( p\)-HBZ oxidation over \( 3\text{Fe}/\text{CeTi-C} \).

**CONCLUSIONS**

3%Fe supported on \( \text{CeO}_2/\text{TiO}_2 \) aerogels are prepared, characterized and evaluated in the oxidation of \( p\)-HBZ in the presence of \( \text{H}_2\text{O}_2 \) at mild conditions. This oxidation could be considered as a Fenton-like reaction due to the production of \( \cdot \text{HO}^- \) from \( \text{H}_2\text{O}_2 \) and Fe supported catalyst. \( 3\text{Fe}/\text{CeTi-C} \) shows the best catalytic properties, at

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**Table 3** | Catalytic behavior of \( 3\text{Fe}/\text{CeTi-C} \) at different reaction temperatures

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>( R_0^a ) (mmol/(g·min))</th>
<th>( p)-HBZ conversion (%) after 10 min</th>
<th>TOC abatement (%) after 1 h</th>
</tr>
</thead>
<tbody>
<tr>
<td>25</td>
<td>0.020</td>
<td>7.0</td>
<td>37</td>
</tr>
<tr>
<td>40</td>
<td>0.081</td>
<td>25</td>
<td>48</td>
</tr>
<tr>
<td>60</td>
<td>0.166</td>
<td>73</td>
<td>52</td>
</tr>
</tbody>
</table>

\( a \)Initial reaction rate.
conditions of pH 3.2, 60 °C and H2O2/p–HBZ molar ratio of 14, compared to the reduced one. This catalyst reaches 0.166 mmol/(g·min) of initial reaction rate, 73% of p–HBZ conversion after 10 min and 52% of TOC abatement after 1 h. CeO2 plays an important role in these good catalytic properties; this closely relies on the synergistic effect with TiO2 allowing better O2 availability to active sites due to the redox cycle of Ce4+/Ce3+. Further studies are required to characterize the catalyst after reaction and to check the catalyst stability in a continuous reactor. One important direction for our future work would be a greater focus on the Fenton-like oxidation of real wastewaters using supported Fe catalysts.

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