Decomposition of hydrogen peroxide in a catalytic fluidized-bed reactor

Shanshan Chou, Chihpin Huang

Institute of Environmental Engineering, National Chiao Tung University, Hsinchu 30039, Taiwan

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Abstract

The decomposition of H_2O_2 by a novel supported γ-FeOOH catalyst was performed in a continuous fluidized-bed reactor. This catalyst has been successfully used in the treatment of organic contaminants with H_2O_2 in our previous work. In this study, we attempted to determine the effects of pH, H_2O_2 concentration, and catalyst concentration on the decomposition of H_2O_2. An approach, we regarded this reactor as a continuous-flow stirred-tank reactor, was applied to investigate the kinetic behavior. At low H_2O_2 concentration, the decomposition rate of H_2O_2 was found to be proportional to both H_2O_2 and catalyst concentrations. At high H_2O_2 concentration, however, the rate decreased with the increasing H_2O_2 concentration. This can be explained by the substrate inhibition model. The large difference in the observed first-order rate constants under various pH values was also modeled. The model agreed well with the experimental results. ©1999 Elsevier Science B.V. All rights reserved.

Keywords: Iron oxide; Hydrogen peroxide; Heterogeneous catalysis; Fluidized bed

1. Introduction

Hydrogen peroxide has been found to be useful in wastewater treatment [1,2] and in soil remediation [3,4]. It is a powerful oxidant for contaminants working either alone or in conjunction with a catalyst [4]. The most common homogeneous catalyst is ferrous iron. When combined with H_2O_2, it is well known as Fenton’s reagent [5]; heterogeneous catalysts involve metal oxides, and supported metal oxides [6]. Recently, the application using iron oxide catalyst has been studied extensively [3,6–9]. Goethite, hematite, semicrystalline, and ferrihydrite have been used as catalysts to treat the organic contaminants [3,7,8]. In our previous work, we developed a novel supported γ-FeOOH catalyst and proved that it can effectively remove benzoic acid and 2,4,6-trichlorophenol [9]. All the results indicate that the removal of contaminants is related to the catalytic decomposition of H_2O_2 by iron oxide. Due to this important role, the catalytic decomposition of H_2O_2 deserves further investigation.

The continuous-flow stirred-tank reactor (CSTR) has been considered as the most attractive reactor for studying the kinetics of solid catalyzed reaction [10]. Most of the studies mentioned above, however, were performed in the batch mode. To prevent the catalyst from any damage due to mechanical mixing, we selected a fluidized-bed reactor (FBR) to conduct experiments. The performance in circulating FBR is similar to that in CSTR when the recycle ratio is large enough [10,11]; the method has been extensively applied in
Table 1
Properties of the catalyst

<table>
<thead>
<tr>
<th>Parameters</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Iron content (g kg(^{-1}))</td>
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</tr>
<tr>
<td>Total surface concentration of iron(^a) (g kg(^{-1}))</td>
<td>95</td>
</tr>
<tr>
<td>Bulk density (g cm(^{-3}))</td>
<td>1.11</td>
</tr>
<tr>
<td>Dry density (g cm(^{-3}))</td>
<td>1.70</td>
</tr>
<tr>
<td>Average particle size (mm)</td>
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</tr>
<tr>
<td>Specific surface area (m(^2) g(^{-1}))</td>
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</tr>
<tr>
<td>Surface site (mole g(^{-1}))</td>
<td>(5.89 \times 10^{-4})</td>
</tr>
<tr>
<td>(pK_a)</td>
<td>5.3</td>
</tr>
<tr>
<td>(pK_{a2})</td>
<td>8.8</td>
</tr>
<tr>
<td>(pH_{pzc}) (point of zero charge)(^b)</td>
<td>7.05</td>
</tr>
</tbody>
</table>

\(^a\) Total surface concentration of iron on the catalyst = iron content of catalyst – iron content of support.

\(^b\) \(pH_{pzc} = (pK_{a1} + pK_{a2})/2\).

heterogeneous catalysis due to its high efficiency in mass transfer [10].

In this study, we attempted to evaluate the performance of the continuous circulating FBR with the supported \(\gamma\)-FeOOH catalyst. The effects of pH, \(H_2O_2\) concentration and catalyst concentration on the decomposition of \(H_2O_2\) were studied.

2. Experimental

2.1. Catalyst preparation

A novel catalyst, iron oxide on a brick grain support, was developed in the following manner [12]. The brick grains were packed in a 6.1 l (6.8 cm \( \times \) 170 cm-H) FBR as carriers. To maintain a low supersaturation condition for heterogeneous nucleation of iron oxide, 3.5 mM \(H_2O_2\) (Union Chemical) and 7.0 mM FeSO\(_4\) (Merck) were fed continuously into the reactor bottom at 24 (\(\pm\) 4)°C. The pH of the solution was controlled at 3.5 to prevent Fe(OH)\(_3\) precipitation. The crystals were allowed to grow on the surfaces of brick grains for 1 week. Table 1 lists the properties of the catalyst prepared from FBR. The number of fluoride-binding surface sites (mole g\(^{-1}\)) was determined following the method of Sigg and Stumm [13]. Intrinsic acidity constants (\(K_{a1}\) and \(K_{a2}\)) were obtained from graphic extrapolation of transformed acid/base titration data to zero surface charge conditions [14]. The major component coated on the catalyst surface was identified as \(\gamma\)-FeOOH with a Mössbauer spectrometer (Austin S-600).

Fig. 1. The schematic diagram of the fluidized-bed reactor.

2.2. Catalytic experiments

All the catalytic experiments were conducted at room temperature (24 \(\pm\) 4°C). The schematic apparatus is shown in Fig. 1. Two bench-scale FBRs were packed with 4 and 2 mm of glass beads on the bottom separately, and then the desired amount of supported \(\gamma\)-FeOOH catalyst grains. The smaller one (2 cm-\(\phi\) \(\times\) 100 cm-H) was applied for most of the experiments and the larger one (3 cm-\(\phi\) \(\times\) 200 cm-H) was used only in part of Section 4.2. The recycle ratio of FBR was kept between 1.5 and 10 (normally above 4) except for trials studying the mixing effect. The superficial velocity was maintained at 40–60 m h\(^{-1}\) with circulation. The applied flow rate and \(H_2O_2\) concentration were determined from the residence time (\(\tau\)) and the desired \(H_2O_2\) dosage, respectively. To maintain a stable pH during the reaction, pH was controlled by regulating the pH of \(H_2O_2\) feed before the experiment. The effluent was collected after 5 \(\tau\) s to insure that the reaction was at steady state [15]. The sample was filtered and titrated with KMnO\(_4\) (Union Chemical) for the analysis of \(H_2O_2\).

3. Theory

In the earlier literature [7,16,17], the catalytic decomposition of hydrogen peroxide with metals or metal oxides has been described by the Weiss mecha-
Table 2
Mechanism proposed for decomposition of H₂O₂ on goethite [18]

\[
\begin{align*}
& \text{Fe}^{3+} \text{OH} + \text{H}_2 \text{O}_2 \rightleftharpoons \text{Fe}^{2+} \text{OH} + \text{H}_2 \text{O}_2 \text{S} \quad \text{(II.1)} \\
& \text{H}_2 \text{O}_2 \rightleftharpoons \text{Fe}^{3+} \text{OH} + \text{H}_2 \text{O} \quad \text{(II.2)} \\
& \text{Fe}^{3+} \text{OH} \rightleftharpoons \text{Fe}^{2+} + \text{H}_2 \text{O}_2 \quad \text{(II.3)} \\
& \text{Fe}^{3+} \text{OH} + \text{H}_2 \text{O}_2 \rightleftharpoons \text{Fe}^{3+} \text{OH} + \text{H}_2 \text{O} + \text{H}_2 \text{O}_2 \quad \text{(II.4)} \\
& \text{HO}_2^- \rightleftharpoons \text{H}^+ + \text{O}_2 \quad \text{(II.5)} \\
& \text{Fe}^{3+} \text{OH} + \text{H}_2 \text{O}_2 \rightleftharpoons \text{Fe}^{3+} \text{OH} + \text{H}_2 \text{O} \left( \text{OH}^- \right) + \text{O}_2 \quad \text{(II.6)} \\
& \text{Fe}^{3+} \text{OH} \rightleftharpoons \text{Fe}^{2+} \text{OH} \quad \text{(II.7)}
\end{align*}
\]

anism, in which the major reaction is:

\[
\text{H}_2 \text{O}_2 + \text{S} \rightarrow \text{OH}^+ + \text{OH}^- + \text{S}^+ \quad \text{(1)}
\]

where \( \text{S} \) denotes the active site on the catalyst surface and \( \text{S}^+ \) represents the oxidized site. Recently, Lin and Gurol [18] has regarded that the Weiss mechanism cannot appropriately explain the decomposition of H₂O₂ by granular goethite. Based on the surface complexation of iron oxide, they proposed another reaction mechanism which is similar to the Fenton-like reaction of \( \text{Fe}^{3+}/\text{H}_2 \text{O}_2 \) system [19]. The H₂O₂ decomposition rate (\( R_H \)) can be expressed as Eq. (2) according to the new reaction mechanism proposed in Table 2:

\[
R_H = \frac{kS_T[\text{H}_2 \text{O}_2]}{1 + K_H[\text{H}_2 \text{O}_2]} \quad \text{(2)}
\]

where \( k = 2k_1k_2k_3/k' \), \( K_H = k_1(k_3 + k_2)/k' \), \( k' = k_3(k_1 + k_2) + k_1k_2a \). \( S_T \) is the total concentration of the surface sites, and \([\text{H}_2 \text{O}_2]\) represents the H₂O₂ concentration in the batch reactor. This equation resembles the classic Langmuir–Hinshelwood equation (L–H equation) [20] in heterogeneous catalysis, where \( k \) and \( K_H \) correspond to the rate constant and equilibrium binding constant [8]. The kinetic model has been verified at pH 7 between 1.1 and 11 mM of \([\text{H}_2 \text{O}_2]\). When \( K_H[\text{H}_2 \text{O}_2] \ll 1 \), Eq. (2) can be reduced to a second-order kinetic expression verified by Lin and Gurol [18]:

\[
R_H = kS_T[\text{H}_2 \text{O}_2] \quad \text{(3)}
\]

4. Results and discussion

In this study, the catalytic experiments were conducted in a circulating FBR, which can be regarded as a CSTR at larger recycle ratio \( (R) \). According to the mass balance of H₂O₂ in the CSTR, the decomposition rate of H₂O₂ \( (R_H) \) can be determined directly from the inlet and outlet H₂O₂ concentrations; the rate is related to its conversion:

\[
R_H = \frac{C_{\text{Hi}} - C_{\text{H}}}{\tau} = \frac{C_{\text{Hi}}X}{\tau} \quad \text{(4)}
\]

where \( X \) is the conversion of H₂O₂, \( C_{\text{Hi}} \) and \( C_{\text{H}} \) denote the inlet and outlet H₂O₂ concentrations at steady state, respectively.

To verify the applicability of Eq. (4), the mixing effect in FBR was investigated by varying \( R \). The result shows that \( R_H \) was independent of \( R \) at pH 7.0 \( (C_{\text{Hi}} = 23.5 \text{ mM}, \ \tau = 13 \text{ min}, \ \text{catalyst concentration} = 167 \text{ g l}^{-1}) \). It may be due to the turbulent flow of numerous oxygen bubbles caused by higher reaction rate at pH 7.0 (as mentioned later). However, at pH 3.5 and pH 5.0, \( R_H \) remained constant when \( R > 0.9 \) but gradually decreased when \( R < 0.9 \). Since a \( R \) value of 0.9 corresponded to 15 m h⁻¹ of superficial velocity under this condition, all of the following experiments were performed at \( R > 1.5 \) and superficial velocity \( > 40 \text{ m h}^{-1} \), which are far above these two critical values (i.e. 0.9 and 15 m h⁻¹).

4.1. Effects of \( \text{H}_2 \text{O}_2 \) and catalyst concentrations

The decomposition of H₂O₂ was conducted with various inlet H₂O₂ concentrations \( (C_{\text{Hi}}) \) at pH values of 3.5, 5.0 and 7.5. The relationship between the conversion of H₂O₂ and \( C_{\text{Hi}} \) is shown in Fig. 2(a). The conversion at steady state decreases with increasing \( C_{\text{Hi}} \) at these three pH conditions. It is also found that, at the same \( C_{\text{Hi}} \), the conversion at pH 7.5 is far larger than that at pH 3.5. To analyze the kinetics, the decomposition rate of H₂O₂ versus the outlet H₂O₂ concentrations \( (C_{\text{H}}) \) was plotted, as shown in Fig. 2(b). In this figure, \( R_H \) is presented as a function of outlet H₂O₂ concentration. It is shown that \( R_H \) is proportional to \( C_{\text{H}} \) at low H₂O₂ concentration, and the catalytic reaction is decreased with the excess H₂O₂ after reaching its maximum. Since oxygen is formed in decomposing H₂O₂, it must first be clarified whether the excess oxygen at high H₂O₂ concentration inhibits the decomposition of H₂O₂. It seems plausible that the adsorption of oxygen would compete with H₂O₂ for the active sites of the catalyst surface, thereby affect the decomposition rate of H₂O₂.
experiment performed with introducing additional air by a small air diffuser, however, shows that increasing dissolved oxygen does not have any effect on the decomposition rate of H$_2$O$_2$. Therefore, the effect of the holdup of gaseous oxygen on the decomposition of H$_2$O$_2$ can be neglected in this reaction system.

Inhibition by excess substrate has been extensively studied in many enzymatic (bio-catalytic) systems [21,22]. Haldane [21] applied a simple model mechanism with regard to substrate inhibition:

$$ E + A \xrightleftharpoons[k_{-el}]{k_{el}} EA \xrightarrow{k_{-e2}} E + \text{Products} \quad (5) $$

$$ \text{EA} + A \xrightleftharpoons[k_{-e3}]{k_{e3}} \text{EA}_2 \quad \text{(dead-end reaction)} \quad (6) $$

where E and A denote enzyme and substrate, respectively. A commonly accepted explanation is that two substrate molecules get stuck together in the same active site (that is, we get an ineffective EA$_2$ complex). In high substrate concentration, the chance of forming ineffective complexes increases. Therefore, we modified the reaction mechanism proposed by Lin and Gurol (as shown in Table 2) by incorporating the substrate inhibition mechanism of enzyme kinetics [21,22]. To derive the rate equation of H$_2$O$_2$ decomposition in our reaction system, the formation of ineffective H$_2$O$_2$–catalyst surface complex (i.e., (H$_2$O$_2$)$_2$–S) is also included

$$ \text{H}_2\text{O}_2{\text{–S}} + \text{H}_2\text{O}_2 \xrightarrow[k_{-i}]{k_i} \text{(H}_2\text{O}_2)_2{\text{–S}} \quad K_I = \frac{k_i}{k_{-i}} \quad (7) $$

where H$_2$O$_2$–S denotes the effective H$_2$O$_2$–catalyst surface complex, and $K_I$ represents the equilibrium binding constant of an ineffective complex (mM$^{-1}$). The steady state concentration of (H$_2$O$_2$)$_2$–S can be expressed, derived from reaction (7), as:

$$ \left[\text{(H}_2\text{O}_2)_2{\text{–S}}\right] = K_I C_H [\text{H}_2\text{O}_2{\text{–S}}] \quad (8) $$

The mass balance equation for the surface sites of the catalyst can be written as Eq. (9) by neglecting the species $\equiv\text{Fe}^{II}$ and $\equiv\text{Fe}^{II}{\cdot}\text{O}_2\text{H}$ (as shown in Table 2) due to the fact that $\equiv\text{Fe}^{II}$ is readily oxidized by H$_2$O$_2$ and $\equiv\text{Fe}^{II}{\cdot}\text{O}_2\text{H}$ is only a transitional state.

$$ S_T = \left[\equiv\text{Fe}^{III}\text{OH}\right] + [\text{H}_2\text{O}_2{\text{–S}}] + \left[\text{(H}_2\text{O}_2)_2{\text{–S}}\right] \quad (9) $$

Therefore, $R_H$ can be derived from a modified L–H equation (the detailed derivation is shown in the Appendix A),

$$ R_H = \frac{k_S I C_H}{1 + K_H C_H (1 + K_I C_H)} \quad (10) $$

which differs from Eq. (2) only in the term $(1 + K_I C_H)$ of the denominator. Note that $C_H$ is used here to denote the outlet H$_2$O$_2$ concentration of FBR at steady state instead of the time-variant H$_2$O$_2$ concentration in the batch reactor (i.e., [H$_2$O$_2$], as indicated in Eq. (2)). Parameters in Eq. (10) can be replaced by the form used in the substrate inhibition model of enzyme kinetics [22].
\[ R_H = \frac{k_H K_H C_H}{1 + K_H C_H (1 + K_1 C_H)} \]  

(11)

where \( k_H = k_{S_T} / K_H \) (mM s\(^{-1}\)). The number of the active sites on the catalyst surface is reduced by the formation of ineffective complexes, which limit the decomposition of \( \text{H}_2\text{O}_2 \). Three parameters (\( k_H, K_H, \) and \( K_1 \)) in the model equation at pH values of 3.5, 5.0 and 7.5 can be determined via the linear transformation of Eq. (11), and the results are listed in Table 3.

\[ \frac{C_H}{R_H} = \frac{1}{k_H K_H} + \frac{1}{k_H C_H} + \frac{K_1}{k_H} C_H^2 \]  

(12)

It shows that \( k_H \) at pH 3.5 (e.g., 0.0355 mM s\(^{-1}\)) is much lower than those at pH 5.0 and pH 7.5 (e.g., 0.267 and 0.445 mM s\(^{-1}\), respectively). Furthermore, \( K_H \) increases but \( K_1 \) decreases with increasing pH. It is observed in Fig. 2(b) that the maxima of \( R_H \) at these pH values all occurred at 36–51 mM of \( \text{H}_2\text{O}_2 \) concentration (\( C_{\text{H,max}} \)), which can also be calculated using:

\[ \frac{dR_H}{dC_H} = 0, C_{\text{H,max}} = \frac{1}{\sqrt{K_H K_1}} \]  

(13)

This model seems to contradict to other observations [6,8,23,24] in which \( R_H \) follows a simple first-order relationship with respect to \( \text{H}_2\text{O}_2 \) concentration. As a matter of fact, the reaction rate with respect to \( \text{H}_2\text{O}_2 \) was found to follow first-order at relatively low \( C_H \) in our previous study [9]. The \( \text{H}_2\text{O}_2 \) concentration that we applied in this study (i.e., 0–120 mM) was much higher than those used in other studies, therefore, inhibition on \( R_H \) at higher \( C_H \) occurred.

To simplify the kinetic behavior, we use a pseudo-first-order relationship to describe the reaction at constant catalyst amount when \( C_H < C_{\text{H,max}} \). The observed first-order rate constant, \( k'_\text{obs} \) (s\(^{-1}\)), can be calculated from the following equation:

\[ k'_\text{obs} = \frac{R_H}{C_H} = \frac{C_{\text{H,i}} - C_H}{C_H \tau} \]  

(14)

Furthermore, experiments were conducted with different catalyst amounts in FBR. The result, shown in Fig. 3, demonstrates that \( k'_\text{obs} \) and the catalyst concentration have a good linear relationship. Therefore, we have concluded that \( R_H \) is proportional to both \( \text{H}_2\text{O}_2 \) and catalyst concentrations at low \( C_H \), which corresponds to Eq. (3). The iron content of the catalyst surface is believed to be the key factor in catalyzing the decomposition of \( \text{H}_2\text{O}_2 \) [6,18]. We thus define \( k_{\text{obs}} \) as below, because the iron content is proportional to the catalyst concentration:

\[ k_{\text{obs}} = \frac{k'_\text{obs}}{[\text{Fe}]_T} = \frac{C_{\text{H,i}} - C_H}{[\text{Fe}]_T [\text{Fe}]_T \tau} \]  

(15)

where \([\text{Fe}]_T\) denotes the total surface concentration of iron on the catalyst per volume of FBR.

4.2. Effect of pH

According to Eq. (15), \( k_{\text{obs}} \) can be more accurately estimated by performing experiments under different \( \tau \)s. The change in \((C_{\text{H,i}} - C_H)/C_H/[\text{Fe}]_T\) with increasing \( \tau \) at different pH conditions is depicted in Fig. 4, in which a good linear relationship between the two is shown. These slopes \((k_{\text{obs}})\) are listed in Table 4, showing that \( k_{\text{obs}} \) increased with increasing pH and became much larger when pH exceeded 5.5. As indicated in Table 2, \( \equiv \text{Fe}^{3+}\text{OH} \) was used to denote the active site of catalyst surface to simplify the reaction mechanism. As a matter of fact, the iron oxide contain three surface species: \( \equiv \text{Fe}^{3+}\text{OH}^+ \), \( \equiv \text{Fe}^{3+}\text{OH} \) and \( \equiv \text{Fe}^{3+}\text{O}^- \). The equilibrium of surface chemistry [25] concerning these three species can be expressed as:

\[ \equiv \text{FeOH}^+ \Leftrightarrow \equiv \text{FeOH} + \text{H}^+ \quad K_{a1} \]  

(16)

\[ \equiv \text{FeOH} \Leftrightarrow \equiv \text{FeOH}^- + \text{H}^+ \quad K_{a2} \]  

(17)
Table 3
Three kinetic parameters in Eq. (11)\textsuperscript{a}

<table>
<thead>
<tr>
<th>pH</th>
<th>(k_H) (\text{mM s}^{-1})</th>
<th>(K_H) (\text{mM}^{-1})</th>
<th>(K_I) (\text{mM}^{-1})</th>
<th>(C_{H_{\text{max}}}) (mM)</th>
<th>(\alpha^+)</th>
<th>(\alpha^0)</th>
<th>(\alpha^-)</th>
</tr>
</thead>
<tbody>
<tr>
<td>3.5</td>
<td>0.0355</td>
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<td>3.36 \times 10^{-2}</td>
<td>51</td>
<td>0.984</td>
<td>0.016</td>
<td>7.82 \times 10^8</td>
</tr>
<tr>
<td>5.0</td>
<td>0.267</td>
<td>1.95 \times 10^{-2}</td>
<td>3.16 \times 10^{-2}</td>
<td>40</td>
<td>0.666</td>
<td>0.334</td>
<td>5.29 \times 10^{-3}</td>
</tr>
<tr>
<td>7.5</td>
<td>0.445</td>
<td>2.60 \times 10^{-2}</td>
<td>2.99 \times 10^{-2}</td>
<td>36</td>
<td>0.006</td>
<td>0.947</td>
<td>0.047</td>
</tr>
</tbody>
</table>

\textsuperscript{a} Calculation of \(\alpha^+\), \(\alpha^0\), and \(\alpha^-\) is based on \(pK_{a1} = 5.3\) and \(pK_{a2} = 8.8\), as shown in Table 1.

![Graph showing the relationship between \((C_{Hi} - C_{H})/C_{H}\) and \([\text{Fe}]\) T with different pH values.](image)

Table 4
Various \(k_{\text{obs}}\) values under different pH values

<table>
<thead>
<tr>
<th>pH</th>
<th>(k_{\text{obs}}) (M\text{s}^{-1})</th>
<th>pH</th>
<th>(k_{\text{obs}}) (M\text{s}^{-1})</th>
</tr>
</thead>
<tbody>
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<td>3.87 \times 10^{-4}</td>
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<td>6.7</td>
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<td>7.5</td>
<td>1.10 \times 10^{-2}</td>
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</tr>
</tbody>
</table>

\textsuperscript{a} Calculated from Fig. 4.

\textsuperscript{b} Experiments were conducted in the larger FBR with 590 g\text{gl}^{-1} of catalyst (\(C_{Hi} = 23.5 \text{mM}\), \(m = 167 \text{g} \text{l}^{-1}\), \([\equiv \text{Fe}]\) \(T = 167 \text{g} \text{l}^{-1} \times 0.095 \text{g} \text{Fe/g catalyst} = 15.9 \text{g} \text{Fe/l} = 0.283 \text{M}\).

Thus, \([\equiv \text{Fe}^{III} \text{OH}^+\equiv]\) and \([\equiv \text{Fe}^{III} \text{O}^-\equiv]\) can be expressed in terms of \([\equiv \text{Fe}^{III} \text{OH}\equiv]\) without considering the electrostatic interaction, as shown in Eqs. (18) and (19):

\[
[\equiv \text{Fe}^{III} \text{OH}^+] = [\equiv \text{Fe}^{III} \text{OH}] [H^+] / K_{a1} \tag{18}
\]

\[
[\equiv \text{Fe}^{III} \text{O}^-] = [\equiv \text{Fe}^{III} \text{OH}] K_{a2} / [H^+] \tag{19}
\]

The variation in \(k_{\text{obs}}\) with pH may be explained by the changes in the proportion of these three different surface species. Since each species maintains a different level of binding strength with H\(_2\)O\(_2\), according to the surface complexation theory [25,26], the binding strength between H\(_2\)O\(_2\) and \(\gamma\)-FeOOH may be altered when pH is changed.

Next, experimental results were modeled using an approach similar to that of Butler and Hayes [27]. Assuming that three surface species have different reaction rates with respect to the decomposition of H\(_2\)O\(_2\),
we can write the rate equation as:

$$R_H = k_{\text{obs}} \left[ \equiv \frac{\text{Fe}}{\text{T}} \right] C_H = \left( k^+ \left[ \equiv \frac{\text{Fe}^{\text{III}} \text{OH}^+}{2} \right] + k^0 \left[ \equiv \frac{\text{Fe}^{\text{III}} \text{OH}}{2} \right] + k^- \left[ \equiv \frac{\text{Fe}^{\text{III}} \text{O}^-}{2} \right] \right) C_H \quad (20)$$

where $k^+$, $k^0$, and $k^-$ represent the rate constants associated with $\equiv \frac{\text{Fe}^{\text{III}} \text{OH}^+}{2}$, $\equiv \frac{\text{Fe}^{\text{III}} \text{OH}}{2}$, and $\equiv \frac{\text{Fe}^{\text{III}} \text{O}^-}{2}$, respectively. Eq. (20) can be transformed to:

$$k_{\text{obs}} = k^+ \alpha^+ + k^0 \alpha^0 + k^- \alpha^- \quad (21)$$

where $\alpha^+ = [\equiv \frac{\text{Fe}^{\text{III}} \text{OH}^+}{2}] / [\equiv \frac{\text{Fe}}{\text{T}}]$, $\alpha^0 = [\equiv \frac{\text{Fe}^{\text{III}} \text{OH}}{2}] / [\equiv \frac{\text{Fe}}{\text{T}}]$, and $\alpha^- = [\equiv \frac{\text{Fe}^{\text{III}} \text{O}^-}{2}] / [\equiv \frac{\text{Fe}}{\text{T}}]$. These three ionization fractions ($\alpha^+$, $\alpha^0$, $\alpha^-$) of surface hydroxyl group can be calculated from Eqs. (18) and (19). The $k_{\text{obs}}$ values in Table 4 were fitted with Eq. (21) using multiple regression of statistical techniques. Three rate constants with large differences were obtained: $k^+ = 8.67 \times 10^{-5} \text{M}^{-1} \text{s}^{-1}$, $k^0 = 6.75 \times 10^{-3} \text{M}^{-1} \text{s}^{-1}$ and $k^- = 0.109 \text{M}^{-1} \text{s}^{-1}$ ($r^2 = 0.953$). To test the significance of regression, we calculated the statistic $F$ from the analysis of variance. Since $F = 40.1 > F_{0.05,(3,5)} = 5.4$, we conclude that $\alpha^+$, $\alpha^0$, and $\alpha^-$ contribute significantly in predicting $k_{\text{obs}}$. The experimental result fitted with model parameters is shown in Fig. 5, which indicates that the model agrees well with the experimental results. The change of $K_R$ (Table 3) also demonstrates that H$_2$O$_2$ favors the sites bearing negative charge. This can be explained by the conclusion of Wallace [28]: H$_2$O$_2$ may form strong complexes with weak base sites such as $\equiv \frac{\text{Fe}^{\text{III}} \text{O}^-}{2}$.

5. Conclusions

From Section 4 we have come to the following conclusions.

1. The decomposition rate of H$_2$O$_2$ is proportional to both $C_H$ and catalyst concentration at low $C_H$, but decays at high $C_H$, which can be interpreted using the modified Langmuir–Hinshelwood equation by incorporating the substrate inhibition model.

2. The effect of pH on $k_{\text{obs}}$ can be attributed to the large differences in reaction rates between H$_2$O$_2$ and three surface species of iron oxide, i.e. $\equiv \frac{\text{Fe}^{\text{III}} \text{OH}^+}{2}$, $\equiv \frac{\text{Fe}^{\text{III}} \text{OH}}{2}$, and $\equiv \frac{\text{Fe}^{\text{III}} \text{O}^-}{2}$.

6. Notation

- $C_{\text{Hi}}, C_H$: inlet and outlet H$_2$O$_2$ concentrations of FBR at steady state (mM)
- $C_{H,\text{max}}$: outlet H$_2$O$_2$ concentration where maximum $R_H$ occurs (mM)
- $[\equiv \frac{\text{Fe}}{\text{T}}]$: total surface concentration of iron on the catalyst per volume of FBR (M)
- $S_T$: total concentration of active surface sites (mM)
- $k$: chemical reaction rate constant in Eqs. (2) and (10) (mM s$^{-1}$)
- $k^+, k^0, k^-$: rate constants associated with $\equiv \frac{\text{Fe}^{\text{III}} \text{OH}^+}{2}$, $\equiv \frac{\text{Fe}^{\text{III}} \text{OH}}{2}$, and $\equiv \frac{\text{Fe}^{\text{III}} \text{O}^-}{2}$ (M$^{-1}$ s$^{-1}$)
- $k_H$: chemical reaction rate constant in Eq. (11) (mM s$^{-1}$)
- $k'_{\text{obs}}$: observed first-order rate constant in decomposing H$_2$O$_2$ (Eq. (14)) (s$^{-1}$)
- $k_{\text{obs}} k'_{\text{obs}} / [\equiv \frac{\text{Fe}}{\text{T}}]$: (M$^{-1}$ s$^{-1}$)
- $K_I$: equilibrium binding constant of an ineffective surface complex in reaction (7) (mM$^{-1}$)
- $K_H$: equilibrium constant in Eqs. (2), (10) and (11) (mM$^{-1}$)
- $m$: catalyst weight per volume of solution (g l$^{-1}$)
- $R_H$: decomposition rate of H$_2$O$_2$ (mM s$^{-1}$)
\[ \alpha^+ = \left[ \text{Fe}^{III}\text{OH}^+ \right] \left[ \text{Fe}^{II} \right] \]
\[ \alpha^0 = \left[ \text{Fe}^{III}\text{OH} \right] \left[ \text{Fe}^I \right] \]
\[ \alpha^- = \left[ \text{Fe}^{III}\text{O}^- \right] \left[ \text{Fe}^I \right] \]
\[ \tau = \text{residence time of FBR (min)} \]

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Appendix A. (detailed derivation of Eq. (10))

Since the modified mechanism incorporates the substrate inhibition model with the mechanism proposed by Lin and Gurol [18], both reaction (7) and reactions (II.1)–(II.7) (as shown in Table 2) are included in this study. The assumptions given by Lin and Gurol [18] were used in simplifying the derivation of the kinetic equations. According to the modified mechanism, the major reactions responsible for the decomposition of \( \text{H}_2\text{O}_2 \) are reactions (II.1), (7), and (II.4). The decomposition rate of \( \text{H}_2\text{O}_2 \), \( R_H \), can be accordingly presented as:

\[ R_H = k_1 \left[ \text{Fe}^{III}\text{OH} \right] C_H - k_{1a} \left[ \text{H}_2\text{O}_2-S \right] + k_i \left[ \text{H}_2\text{O}_2-S \right] C_H - k_{-i} \left[ \text{H}_2\text{O}_2 \right] + k_4 \left[ \text{Fe}^{II} \right] C_H \quad (A.1) \]

The steady state concentration of \( \text{H}_2\text{O}_2-S \) can be derived from reaction (7) as:

\[ k_i \left[ \text{H}_2\text{O}_2-S \right] C_H = k_{-i} \left[ \text{H}_2\text{O}_2 \right] \quad (A.2) \]

Accordingly, Eq. (A.1) can be simplified to

\[ R_H = k_1 \left[ \text{Fe}^{III}\text{OH} \right] C_H - k_{1a} \left[ \text{H}_2\text{O}_2-S \right] + k_4 \left[ \text{Fe}^{II} \right] C_H \quad (A.3) \]

The steady state concentration of \( \text{H}_2\text{O}_2-S \) can be derived from reactions (II.1), (7), and (II.2) as:

\[ \left[ \text{H}_2\text{O}_2-S \right] = \frac{k_1 \left[ \text{Fe}^{III}\text{OH} \right] C_H + k_{2a} \left[ \text{Fe}^{II}\text{O}_2\text{H} \right]}{(k_{1a} + k_2)} \quad (A.4) \]

Since \( K_1 = k_0/k_{-1} \), Eq. (A.2) can be further simplified to Eq. (8). At steady state, \( \equiv \text{Fe}^{III}\text{O}_2\text{H} \) is given by Eq. (A.5) based on reactions (II.2) and (II.3).

\[ \equiv \text{Fe}^{II}\text{O}_2\text{H} = \frac{k_2 \left[ \text{H}_2\text{O}_2-S \right]}{k_3 + k_{2a}} \quad (A.5) \]

Eq. (A.4) can be transformed into Eq. (A.6) by introducing Eq. (A.5).

\[ \left[ \text{H}_2\text{O}_2-S \right] = \frac{k_1 \left( k_3 + k_{2a} \right) \left[ \text{Fe}^{III}\text{OH} \right] C_H}{k_3 \left( k_{1a} + k_2 \right) + k_{1a} k_{2a}} \quad (A.6) \]

From reactions (II.3) and (II.4), the \( \equiv \text{Fe}^{II} \) at steady state condition is:

\[ \equiv \text{Fe}^{II} = \frac{k_3 \left[ \equiv \text{Fe}^{II}\text{O}_2\text{H} \right] C_H}{k_4 C_H} = \frac{k_3 k_2 \left[ \text{H}_2\text{O}_2-S \right]}{k_4 \left( k_3 + k_{2a} \right) C_H} \quad (A.7) \]

Substituting Eqs. (A.6) and (A.7) into Eq. (A.3), one will obtain:

\[ R_H = \frac{2k_1 k_2 k_3 \left[ \equiv \text{Fe}^{III}\text{OH} \right] C_H}{k_3 \left( k_{1a} + k_2 \right) + k_{1a} k_{2a}} \quad (A.8) \]

Since \( \equiv \text{Fe}^{II} \) is oxidized rapidly by \( \text{H}_2\text{O}_2 \) and \( \equiv \text{Fe}^{II}\text{O}_2\text{H} \) is only a transitional state, \( \equiv \text{Fe}^{III}\text{OH} \) and \( \equiv \text{Fe}^{II}\text{O}_2\text{H} \) are expected to be very low. The mass balance equation for the surface sites of the catalyst can be shown to be

\[ \equiv \text{Fe}^{III}\text{OH} = S_T - \left[ \text{H}_2\text{O}_2-S \right] + \left[ \text{H}_2\text{O}_2 \right] \quad (A.9) \]

Substituting Eqs. (8) and (A.6) into Eq. (A.9), one will obtain:

\[ \equiv \text{Fe}^{III}\text{OH} = \frac{S_T}{1 + K_H C_H (1 + K_1 C_H)} \quad (A.10) \]

where \( K_H = k_1 \left( k_3 + k_{2a} \right) / k' \) and \( k' = k_3 \left( k_{1a} + k_2 \right) + k_{1a} k_{2a} \). Finally, Eq. (A.8) can be transformed into Eq. (10) by introducing Eq. (A.10).

\[ R_H = \frac{k S_T C_H}{1 + K_H C_H (1 + K_1 C_H)} \quad (10) \]

where \( k = 2k_1 k_2 k_3 / k' \).

References