COD removal from phenol solution by heterogeneous Fenton reaction using Fe$_2$O$_3$/SiO$_2$ catalysts: Effects of calcination temperature on the catalyst properties

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The Fe$_2$O$_3$/SiO$_2$ catalysts have been prepared by an impregnation method and calcined at different temperatures (350, 400, and 450°C). The three obtained catalysts are characterized by X-ray powder diffraction (XRD), temperature programmed reduction (TPR), scanning electron microscopy (SEM) and BET. The results showed that the increase of the calcination temperature promoted the dispersion of Fe particles on the surface of the SiO$_2$ support, which results in the change of the BET surface area, the average pore size, and the pore volume of the Fe$_2$O$_3$/SiO$_2$ catalysts. According to the catalytic reaction results, the Fe$_2$O$_3$/SiO$_2$ catalyst calcined at 400°C show the higher catalytic activities than others, and the COD removal is found to be about 64.6% within 60 min, pH 3, 100 μL of H$_2$O$_2$ in a 50 mL phenol solution.

**Keywords:** Catalyst preparation, Calcination temperature, Catalyst characterization, Phenol solution, COD removal, Reaction conditions

Industrial processes generate various wastewater containing organic pollutants, which has become a major social and economic problem. Phenolic wastewater needs to be treated before its release$^{1-3}$. The conventional biological treatment is often the most economical method, and it is considered to be environmental friendly$^4$. However, the utilization is restricted because of the biorecalcitrant and acute toxicity of phenols$^1$. At the same time, the phenol is usually chosen as "model" molecule on the studies of the catalytic degradation of organic compounds in diluted aqueous medium$^3$.

Advanced oxidation processes (AOPs) have been the highly competitive innovative wastewater treatment methods for the removal of biorecalcitrant compounds$^5-7$. One of the most promising AOPs is based on the use of the Fenton reagent (consists of iron ions and H$_2$O$_2$)$^3,8,9$, which induce the formation of hydroxyl radicals (·OH). The ·OH is considered as the most reactive with highest oxidation potential of 2.33 V compared to other oxidizing agents such as O$_3$, or KMnO$_4$ whose oxidation potential are 2.07, and 1.67 V, respectively$^{10,11}$. As well as the ·OH conduces to complete degradation of phenol easily to CO$_2$ and H$_2$O at low temperature$^3,12$, the relevant reaction is as follow:

$$\text{C}_6\text{H}_5\text{OH} + \cdot\text{OH} \rightarrow \text{CO}_2 + \text{H}_2\text{O} \quad \ldots (1)$$

The conventional Fenton system is a homogeneous reaction carried out at room temperature with normal pressure. Although the homogeneous Fenton reagent is effective for oxidizing and degrading phenol, there are problems with its practical application because the Fe ions are difficult to remove from the reaction medium at the end of each experimental run. To overcome these drawbacks, the heterogeneous catalyst has been reported in the last decades$^{4,13,14}$. The mechanism of heterogeneous Fenton reaction is presented as follows$^{12,15,16}$:

$$\text{S-Fe}^{3+} + \text{H}_2\text{O}_2 \rightarrow \text{S-Fe}^{2+} + \text{HO}_2^- + \text{H}^+ \quad \ldots (2)$$

$$\text{S-Fe}^{2+} + \text{H}_2\text{O}_2 \rightarrow \text{S-Fe}^{3+} + \text{HO}^- + \cdot\text{OH} \quad \ldots (3)$$

where S stands for the catalyst’s surface.

Many methods have been reported in the literature for the preparation of heterogeneous catalyst. In the process of the catalysts preparation, the calcination temperature plays an important role which affects the morphology, the specific surface area and the state of surface species of the catalyst. Usually, SiO$_2$, ZnO, and other stable oxides act as textural support, i.e., they stabilize iron phases against sintering during the calcination process$^{17,18}$.

**COD** describes the organic content that is susceptible to oxidation by a strong chemical agent, and this parameter reflects commonly the organic contaminant amount in diluted aqueous medium.

In this paper, Fe$_2$O$_3$/SiO$_2$ catalysts calcined at different temperatures were prepared by the impregnation method, and the physical and chemical properties of the catalysts were investigated by XRD, TPR, SEM, and BET. The catalytic activities have been evaluated by the COD removal in the process of the degradation of the phenol solution. The influences of several parameters on the COD removal of the phenol solution were studied such as H$_2$O$_2$ amount,
the initial pH of the solution, reaction time, and catalyst calcination temperature.

**Experimental Section**

**Materials**

The analytical grade Fe(NO₃)₃·9H₂O, phenol were purchased from Tianjin Fu Chen Chemical Reagent Factory, China. SiO₂ was purchased from Qingdao Haiyang Chemical Co., Ltd, China. H₂O₂ in a 30 wt% aqueous solution was purchased from Wuxi City Yasheng Chemical Co., Ltd, China.

**Preparation of the catalysts**

Supported Fe₂O₃/SiO₂ catalysts with a Fe content of 4 wt% were prepared by impregnating the SiO₂ support with an aqueous solution of Fe(NO₃)₃·9H₂O. In a typical preparation, the SiO₂ support was impregnated with Fe(NO₃)₃·9H₂O aqueous solution for 12 h, and the mixture was dried at 120°C overnight in air and then calcined in air at 350, 400, and 450°C for 4 h, respectively.

**Characterization methods**

The XRD patterns were recorded on a Philips PW3040/60 automatic powder diffractometer using Cu Ka radiation at 40 kV and 40 mA. The patterns were collected in a 2θ range from 15° to 80°.

The hydrogen temperature programmed reduction (H₂-TPR) experiments were performed to determine the reducibility of the catalyst samples. A desired amount of the samples (50 mg) was placed in a quartz reactor (i.d. = 6 mm) and pretreated in a flow of N₂ (30 mL/min) at 100°C for 1 h, and then cooled to room temperature. A gas mixture of H₂ (5%) – N₂ (95%) was then passed (30 mL·min⁻¹) through the reactor. The temperature was increased from room temperature to 800°C at a heating rate of 10°C min⁻¹. A thermal conductivity detector (TCD) was employed to measure the hydrogen consumption during the reduction at the outlet of the reactor.

The BET surface area of the samples were calculated from nitrogen adsorption-desorption isotherm data obtained at -195.7°C on Autosorb-1 (Quantachrome Instruments), and the pore volume were determined from the adsorbed amount at a relative pressure P/P₀ of 0.99.

The SEM images were taken in a field emission scanning electron microscope (Hitachi S-4800).

**Determination of phenol degradation**

Degradation of phenol solution was carried out in a stirring round bottom flask in a water bath and under atmospheric pressure. Typically, 50 mL of aqueous phenol solution (with initial concentration of 0.125 g·L⁻¹, the pH was adjusted by using 1.0 mol·L⁻¹ H₂SO₄) was added to 0.5 g of Fe₂O₃/SiO₂ catalyst by adjusting pH to the desired value for each experimental run. The reactions were carried out at 30°C, respectively.

The phenol degradation effect was evaluated by the COD removal of phenol solution, and the COD removal was calculated as follows:

\[
\text{COD removal} = \frac{\text{COD}_B - \text{COD}_A}{\text{COD}_B} \times 100\%
\]

COD_B and COD_A are the COD before and after degradation of phenol solution.

Chemical oxygen demand (COD) was analyzed according to the Standard Methods (1989, i.e. Dichromate reflux method)²⁹, and the pH value were measured using a digital pH meter (pHS-3C, Shanghai Leici Instrument Factory, China).

**Results and Discussion**

**Catalyst characterization**

The various calcination temperatures Fe₂O₃/SiO₂ catalysts were prepared by an impregnation method for catalytic degradation of phenol solution evaluated by the COD removal and characterized by XRD, TPR, SEM, and BET techniques for exploring the composition and properties of the catalysts.

**XRD characterizations of Fe₂O₃/SiO₂ catalysts**

Figure 1 shows the XRD patterns of Fe₂O₃/SiO₂ catalysts calcined at different temperature. The only detectable phase identified in the diffraction patterns.

![Fig. 1 — XRD patterns of Fe₂O₃/SiO₂ catalysts calcined at different temperatures for 4 h.](image-url)
of the catalysts is hematite (α-Fe₂O₃), which has characteristic diffraction peaks at 2θ values of 24.2°, 33.2°, 35.6°, 40.9°, 49.5°, 54.1°, 62.4°, and 64.0°. It is observed that the diffraction peak intensity of α-Fe₂O₃ decreases gradually with the calcination temperature rising from 350 to 450°C, which could be due to decreasing crystallite size or promoting the dispersion of Fe particles on the surface of the catalysts.

**Reduction behavior of Fe₂O₃/SiO₂ catalysts**

Reduction of pure hematite by hydrogen to metal iron is a complex event that can proceed in different routes via intermediate oxides. The possible reduction reactions, involving hematite and the other derived oxides, have been written below:

\[
\begin{align*}
3\text{Fe}_2\text{O}_3 + \text{H}_2 & \rightarrow 2\text{Fe}_3\text{O}_4 + \text{H}_2\text{O} \quad \text{… (4)} \\
3\text{Fe}_2\text{O}_3 + 3\text{H}_2 & \rightarrow 6\text{FeO} + 3\text{H}_2\text{O} \quad \text{… (5)} \\
\text{Fe}_2\text{O}_3 + 3\text{H}_2 & \rightarrow 2\text{Fe} + 3\text{H}_2\text{O} \quad \text{… (6)} \\
\text{Fe}_2\text{O}_3 + \text{H}_2 & \rightarrow 3\text{FeO} + \text{H}_2\text{O} \quad \text{… (7)} \\
\text{Fe}_2\text{O}_3 + 4\text{H}_2 & \rightarrow 3\text{Fe} + 4\text{H}_2\text{O} \quad \text{… (8)} \\
\text{FeO} + \text{H}_2 & \rightarrow \text{Fe} + \text{H}_2\text{O} \quad \text{… (9)}
\end{align*}
\]

Figure 2 shows the TPR profiles of Fe₂O₃/SiO₂ catalysts with various calcination temperatures. One can see that no reduction peak is observed for the pure SiO₂ support, indicating that single component SiO₂ cannot be easily reduced by H₂. For the Fe₂O₃/SiO₂ catalyst calcined at 350°C, three peaks with maxima at about 453°C (α), 579°C (β), and 678°C (γ) are observed. A similar phenomenon has also been observed by many researchers²⁰-²³. The α peak could be assigned to the reduction of Fe₂O₃ species²¹,²². With increasing calcination temperatures, the α peak are broader and broader, which indicates that there are more Fe species are reduced. Since the load of the Fe is certain for each catalyst, this phenomenon signified that Fe₂O₃ should be reduced by a different route (reaction 4, 5 or 6), likely leading directly to metallic iron from hematite phase partly (reaction 6). The β peak could be assigned to the consecutive reduction of concentrated Fe₃O₄²¹,²².

A similar phenomenon to α peak, it was possible that the more Fe₃O₄ was reduced with the increase of the catalyst calcination temperatures (reaction 7 or 8). The γ peak could be assigned to the reduction of FeO species to Fe particles (reaction 9)²¹,²². In the case of the Fe₂O₃/SiO₂ catalyst calcined at 450°C, the γ peak is shorter than that of the other catalysts, which indicates that less of Fe species were reduced, attributed to there were some metallic iron reduced in the above steps. In addition, the low-temperature shift of γ peaks suggests an easier reduction of the Fe₂O₃/SiO₂ catalysts with increasing calcination temperatures. The possible reasons are that the Fe₂O₃/SiO₂ catalyst calcined at 450°C presents the small iron oxide particle size, which were reduced easily. As reported by Arena et al.²⁰, the reduction of Fe₂O₃ particles depends mostly on crystal size²⁰,²³-²⁷. This observation is in accordance with that of the XRD results above.

**Textural properties of the Fe₂O₃/SiO₂ catalysts**

SEM micrographs of the Fe₂O₃/SiO₂ catalysts calcined at different temperatures are shown in Fig. 3. As shown in Fig. 3, for the Fe₂O₃/SiO₂ catalyst calcined at 350°C (Fig. 3 (a1) and (a2)), the aggregates are bigger and have more “grainy attachments” while the other catalyst’s surface seems flat gradually with the increase of calcination temperature. It is obviously that the higher calcination temperature can promote the dispersion of Fe particles on the surface of the catalysts.

Table 1 presents the main characteristic of pure SiO₂ and the Fe₂O₃/SiO₂ catalysts calcined at different temperatures. As shown in Table 1, the BET surface area and the average pore size of the pure SiO₂ is about 365.9 m²·g⁻¹ and 101.1 Å, respectively. For the Fe₂O₃/SiO₂ catalysts calcined at different temperatures, the BET surface area decreases and the average pore size increases with the increase of the catalysts calcination temperature. Similar phenomenon was reported by Rossi et al.²⁸. The
reason may be, as shown in Fig. 3, due to that the increase of calcination temperature could decrease the size of iron oxide particles, which resulted in partial blockage of the pure SiO2 pores, in according with the XRD results that the iron oxide particle size is smaller and smaller with the increase of calcination temperature. However, the pore volume is bigger for the Fe2O3/SiO2 catalyst calcined at 400°C than any other catalysts calcined at different temperatures, which may be attributed to the agglomerated particles on the surface of the catalyst.

Catalytic activity

To explore the effect of the calcination temperature of catalysts on catalytic activity for the degradation of phenol by heterogeneous Fenton reaction, at reaction temperature is 30°C, we investigated the optimal reaction conditions (i.e., H2O2 amount, pH of phenol solution, and reaction time) using the Fe2O3/SiO2 catalyst calcined at 400°C.

<table>
<thead>
<tr>
<th>Calcination temperature (°C)</th>
<th>SBET (m²·g⁻¹)</th>
<th>Pore volume (cm³·g⁻¹)</th>
<th>Average pore size (Å)</th>
</tr>
</thead>
<tbody>
<tr>
<td>350</td>
<td>351.5</td>
<td>0.8708</td>
<td>100.0</td>
</tr>
<tr>
<td>400</td>
<td>344.1</td>
<td>0.8711</td>
<td>101.0</td>
</tr>
<tr>
<td>450</td>
<td>339.2</td>
<td>0.8669</td>
<td>102.0</td>
</tr>
<tr>
<td>Pure SiO2</td>
<td>365.9</td>
<td>0.9277</td>
<td>101.1</td>
</tr>
</tbody>
</table>

Effect of H2O2 amount on the COD removal

The effect of the variation of the H2O2 dosage on the phenol degradation evaluated by COD removal was examined in the range from 20 μL to 200 μL. According to the mechanism of heterogeneous Fenton reaction, i.e. given as reaction (2) and (3), the ·OH radicals essentially formed is involved in the amount of H2O2 in the phenol solution, which induced to a higher COD removal. As a result, the COD removal of phenol solution significantly increases with the H2O2 addition up to 100 μL. However, the COD removal decreased when the amount of H2O2 exceed 100 μL, which was due to redundant depleted potassium dichromate in the process of the analyzing of COD, which lead to the increase of COD in phenol solution; and further conduced to the decrease of COD removal in phenol solution.

Effect of the initial pH on the COD removal

According to the reaction (1) and the heterogeneous Fenton reaction mechanism, the COD removal of the phenol solution eventually depend on the ·OH, and the ·OH is relative to the initial pH of the solution. The initial pH crucially influenced the COD removal of phenol solution with Fe2O3/SiO2 catalyst calcined at 400°C. Experiments were conducted at initial pH 2.0, 2.5, 3.0, 3.5, and 4.0. Results show that the COD removal is about 64.6% at the initial pH 3.0. According to Bayat et al.12,29, at the
initial pH values are lower than 3, the decrease in ·OH radicals production is due to the formation of the complex species \( \text{[Fe(H}_2\text{O)}_6\text{]}^{2+} \), the reaction of which with \( \text{H}_2\text{O}_2 \) is slower than that of \( \text{[Fe(OH)(H}_2\text{O)}_5\text{]}^{+} \). At higher pH, \( \text{Fe}^{3+} \) precipitates as \( \text{Fe(OH)}_3 \), causing \( \text{H}_2\text{O}_2 \) to be decomposed into \( \text{O}_2 \) and \( \text{H}_2\text{O} \). As a result, the COD removal of phenol solution in the heterogeneous Fenton reaction reached the highest value at around the initial pH 3.0 and then decreased with increase in pH.

**Effect of reaction time on the COD removal**

Fixing the amount 100 μL of \( \text{H}_2\text{O}_2 \) and the initial pH 3.0, respectively, we examined the effect of reaction time on the COD removal of phenol solution using \( \text{Fe}_2\text{O}_3/\text{SiO}_2 \) catalyst calcined at 400°C. As illustrated in Fig. 4, the COD removal from the phenol solution increased gradually with increasing reaction time, while the COD removal reached maximum and remain unchanged.

Since the heterogeneous degradation of phenol solution evaluated by the COD removal involving some parameters, such as the \( \text{H}_2\text{O}_2 \) amount, the initial pH of the phenol solution, and catalysts calcination temperature, which play an important role on the phenol degradation. Figure 4 gives a combination effect of those parameters; one can see that the COD removal reached the highest value within 60 min.

**Effect of calcination temperature on the COD removal**

To explore the effect of calcination temperature on the COD removal in heterogeneous Fenton reaction, the best conditions obtained above (100 μL of \( \text{H}_2\text{O}_2 \), the initial pH 3.0, and reaction time was 60 min) were used in the degradation of 50 mL of a 125 mg·L\(^{-1}\) phenol solution. Figure 4 exhibits that the catalytic activities of \( \text{Fe}_2\text{O}_3/\text{SiO}_2 \) catalysts calcined at various temperatures are noticeable difference. Referring to the XRD and TPR results, \( \alpha-\text{Fe}_2\text{O}_3 \) is present in the catalysts. \( \text{Fe}^{3+} \) reacts with \( \text{H}_2\text{O}_2 \) to produce \( \text{Fe}^{2+} \) which speeds up the decomposition of \( \text{H}_2\text{O}_2 \) in phenol solution to form ·OH radicals (reaction 2 and 3). At the same time, the dispersion of Fe particles on the surface of the catalysts is in favor of the catalysts activity. The optimal calcination temperature of the catalysts was 400°C, the COD removal of phenol solution was about 64.6%. As to the other catalysts, low activities were observed regarding COD removal, about 42.5 and 27.1%, respectively. The possible reason is that the heterogeneous catalytic activity is related to the other parameters of the catalyst, such as the BET surface, pore diameter and pore volume. In the present study, the calcination temperatures had effect on those parameters of \( \text{Fe}_2\text{O}_3/\text{SiO}_2 \) catalysts calcined at 350, 400, and 450°C, respectively (Table 1). For the catalyst calcined at 400°C, the slight increase of the pore volume maybe result in the higher catalytic activity than the others.

**Conclusion**

The heterogeneous catalytic oxidation of phenol is investigated and evaluated by the COD removal of the phenol solution using \( \text{Fe}_2\text{O}_3/\text{SiO}_2 \) catalysts calcined at different temperatures (350, 400, and 450°C). The results demonstrate that the calcination temperatures affect the textural properties and the size of catalyst particles, which reflected on the change of the catalytic activity. The highest COD removal (was about 64.6%) can be achieved using the catalyst calcined at 400°C under the optimum operating conditions: the amount of \( \text{H}_2\text{O}_2 \) is 100 μL, the initial pH is 3.0 of the phenol solution, and reaction time is 60 min.

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**References**

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