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COD removal from phenol solution by heterogeneous Fenton reaction using Fe_2O_3/SiO_2 catalysts: Effects of calcination temperature on the catalyst properties

Jianjun Zhao*, Rui Peng, Yupeng Pan & Yan Tao

Department of Applied Chemistry and Environment Engineering,
Bengbu College, Bengbu 233 030, China
E-mail: zhjj0311@126.com

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The Fe_2O_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_2O_3/SiO_2 catalysts. According to the catalytic reaction results, the Fe_2O_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, *p*H 3, 100 µL of H_2O_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_2O_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_2O at low temperature[3,12], the relevant reaction is as follow:

$$C_6H_5OH + \cdot OH \rightarrow CO_2 + H_2O \quad \ldots (1)$$

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 is as follows[12,15,16]:

$$S\text{-}Fe^{3+} + H_2O_2 \rightarrow S\text{-}Fe^{2+} + HO_2\cdot + H^+ \quad \ldots (2)$$

$$S\text{-}Fe^{2+} + H_2O_2 \rightarrow S\text{-}Fe^{3+} + HO^- + \cdot OH \quad \ldots (3)$$

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_2O_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_2O_2 amount, the initial pH of the solution, reaction time, and catalyst calcination temperature.

Experimental Section

Materials

The analytical grade $Fe(NO_3)_3 \cdot 9H_2O$, phenol were purchased from Tianjin Fu Chen Chemical Reagent Factory, China. SiO_2 was purchased from Qingdao Haiyang Chemical Co., Ltd, China. H_2O_2 in a 30 wt% aqueous solution was purchased from Wuxi City Yasheng Chemical Co., Ltd, China.

Preparation of the catalysts

Supported Fe_2O_3/SiO_2 catalysts with a Fe content of 4 wt% were prepared by impregnating the SiO_2 support with an aqueous solution of $Fe(NO_3)_3 \cdot 9H_2O$. In a typical preparation, the SiO_2 support was impregnated with $Fe(NO_3)_3 \cdot 9H_2O$ 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 (H_2-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 N_2 (30 mL/min) at 100ºC for 1 h, and then cooled to room temperature. A gas mixture of H_2 (5%) – N_2 (95%) was then passed (30 $mL \cdot min^{-1}$) 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/P_0 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 $g \cdot L^{-1}$, the *p*H was adjusted by using 1.0 $mol \cdot L^{-1}$ H_2SO_4.) was added to 0.5 g of Fe_2O_3/SiO_2 catalyst by adjusting *p*H 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:

$$\text{COD removal} = \frac{COD_B - COD_A}{COD_B} \times 100\%$$

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)[19], and the *p*H value were measured using a digital *p*H meter (pHS-3C, Shanghai Leici Instrument Factory, China).

Results and Discussion

Catalyst characterization

The various calcination temperatures Fe_2O_3/SiO_2 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 Fe_2O_3/SiO_2 catalysts

Figure 1 shows the XRD patterns of Fe_2O_3/SiO_2 catalysts calcined at different temperature. The only detectable phase identified in the diffraction patterns

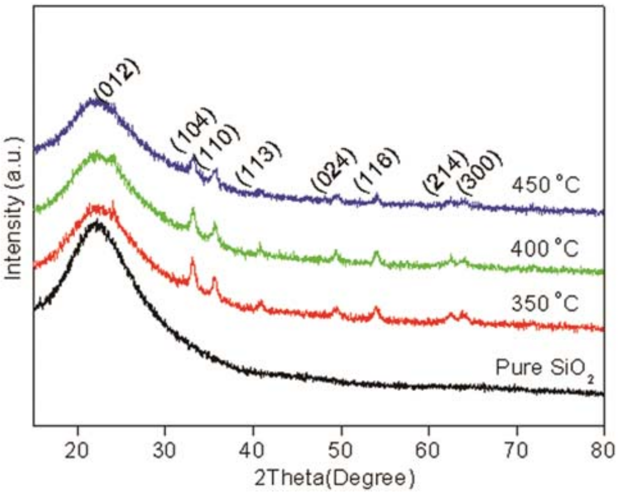

Fig. 1 — XRD patterns of Fe_2O_3/SiO_2 catalysts calcined at different temperatures for 4 h.

of the catalysts is hematite (α-Fe_2O_3), 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-Fe_2O_3 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 Fe_2O_3/SiO_2 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:

$$3Fe_2O_3 + H_2 \rightarrow 2Fe_3O_4 + H_2O \quad \ldots (4)$$

$$3Fe_2O_3 + 3H_2 \rightarrow 6FeO + 3H_2O \quad \ldots (5)$$

$$Fe_2O_3 + 3H_2 \rightarrow 2Fe + 3H_2O \quad \ldots (6)$$

$$Fe_3O_4 + H_2 \rightarrow 3FeO + H_2O \quad \ldots (7)$$

$$Fe_3O_4 + 4H_2 \rightarrow 3Fe + 4H_2O \quad \ldots (8)$$

$$FeO + H_2 \rightarrow Fe + H_2O \quad \ldots (9)$$

Figure 2 shows the TPR profiles of Fe_2O_3/SiO_2 catalysts with various calcination temperatures. One can see that no reduction peak is observed for the pure SiO_2 support, indicating that single component SiO_2 cannot be easily reduced by H_2. For the Fe_2O_3/SiO_2 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 researchers[20-23]. The α peak could be assigned to the reduction of Fe_2O_3 species[21,22]. 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 Fe_2O_3 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 Fe_3O_4[21,22]. A similar phenomenon to α peak, it was possible that the more Fe_3O_4 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 Fe_2O_3/SiO_2 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 Fe_2O_3/SiO_2 catalysts with increasing calcination temperatures. The possible reasons are that the Fe_2O_3/SiO_2 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 Fe_2O_3 particles depends mostly on crystal size[20,23-27]. This observation is in accordance with that of the XRD results above.

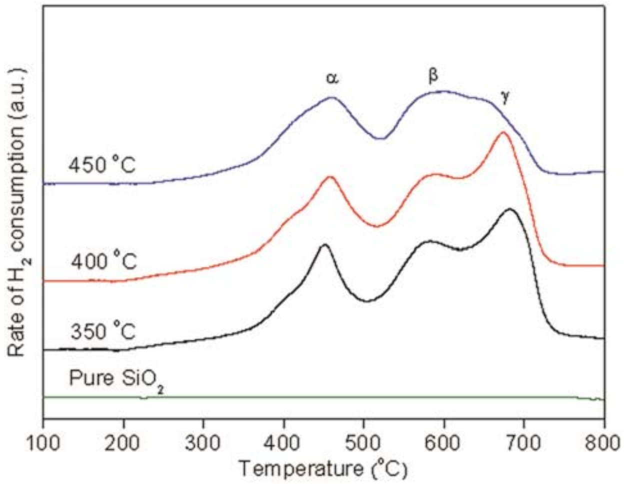

Fig. 2 — H_2-TPR profiles of Fe_2O_3/SiO_2 catalysts calcined at different temperatures for 4 h.

Textural properties of the Fe_2O_3/SiO_2 catalysts

SEM micrographs of the Fe_2O_3/SiO_2 catalysts calcined at different temperatures are shown in Fig. 3 As shown in Fig. 3, for the Fe_2O_3/SiO_2 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

(Fig. 3 (b1), (b2), (c1), and (c2)) 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 SiO_2 and the Fe_2O_3/SiO_2 catalysts calcined at different temperatures. As shown in Table 1, the BET surface area and the average pore size of the pure SiO_2 is about 365.9 $m^2 \cdot g^{-1}$ and 101.1 Å, respectively. For the Fe_2O_3/SiO_2 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

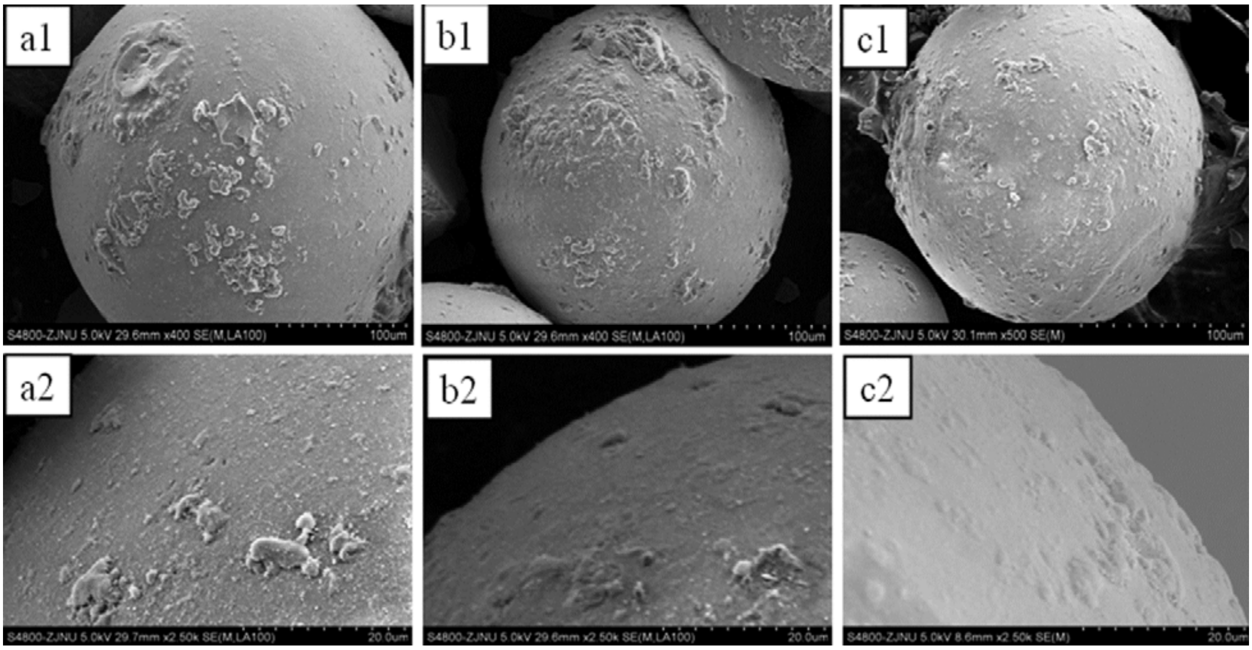

Fig. 3 — SEM micrographs of Fe_2O_3/SiO_2 catalysts calcined at different temperatures, (a1) and (a2): 350°C; (b1) and (b2): 400°C; (c1) and (c2): 450°C.

Table 1 — Results of nitrogen physisorption for the Fe_2O_3/SiO_2 catalysts calcined at different temperatures

Calcination temperature (°C)	S_{BET} ($m^2 \cdot g^{-1}$)	Pore volume ($cm^3 \cdot g^{-1}$)	Average pore size (Å)
350	351.5	0.8708	100.0
400	344.1	0.8711	101.0
450	339.2	0.8669	102.0
pure SiO_2	365.9	0.9277	101.1

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 SiO_2 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 Fe_2O_3/SiO_2 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., H_2O_2 amount, *p*H of phenol solution, and reaction time) using the Fe_2O_3/SiO_2 catalyst calcined at 400°C.

Effect of H_2O_2 amount on the COD removal

The effect of the variation of the H_2O_2 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 H_2O_2 in the phenol solution, which induced to a higher COD removal. As a result, the COD removal of phenol solution significantly increases with the H_2O_2 addition up to 100 μL. However, the COD removal decreased when the amount of H_2O_2 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 *p*H 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 *p*H of the solution. The initial *p*H crucially influenced the COD removal of phenol solution with Fe_2O_3/SiO_2 catalyst calcined at 400°C. Experiments were conducted at initial *p*H 2.0, 2.5, 3.0, 3.5, and 4.0. Results show that the COD removal is about 64.6% at the initial *p*H 3.0. According to Bayat *et al.*[12,29], at the initial *p*H values are lower than 3, the decrease in ·OH radicals production is due to the formation of the complex species $[Fe(H_2O)_6]^{2+}$, the reaction of which with H_2O_2 is slower than that of $[Fe(OH)(H_2O)_5]^{+}$. At higher *p*H, Fe^{3+} precipitates as $Fe(OH)_3$, causing H_2O_2 to be decomposed into O_2 and H_2O[12,30]. As a result, the COD removal of phenol solution in the heterogeneous Fenton reaction reached the highest value at around the initial *p*H 3.0 and then decreased with increase in *p*H.

Effect of reaction time on the COD removal

Fixing the amount 100 μL of H_2O_2 and the initial *p*H 3.0, respectively, we examined the effect of reaction time on the COD removal of phenol solution using Fe_2O_3/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 H_2O_2 amount, the initial *p*H 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 H_2O_2, the initial *p*H 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 Fe_2O_3/SiO_2 catalysts calcined at various temperatures are noticeable difference. Referring to the XRD and TPR results, α-Fe_2O_3 is present in the catalysts. Fe^{3+} reacts with H_2O_2 to produce Fe^{2+} which speeds up the decomposition of H_2O_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 Fe_2O_3/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[27].

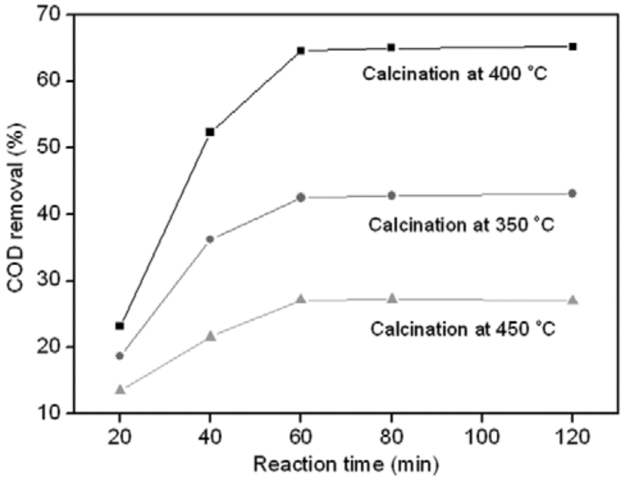

Fig. 4 — Effect of catalysts calcination temperatures on the COD removal of phenol solution, reaction conditions: the amount of H_2O_2 is 100 μL; the initial *p*H is 3.0 and the reaction time is 60 min.

Conclusion

The heterogeneous catalytic oxidation of phenol is investigated and evaluated by the COD removal of the phenol solution using Fe_2O_3/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 H_2O_2 is 100 μL, the initial *p*H is 3.0 of the phenol solution, and reaction time is 60 min.

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