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Catalytic oxidation of phenol in wastewater — A new application of the amorphous Fe₇₈Si₉B₁₃ alloy

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The amorphous $Fe_{78}Si_9B_{13}$ alloy was used as a heterogeneous Fenton catalyst in the process of phenol degradation. The influences of main operating parameters such as reaction temperature, catalyst amount, hydrogen peroxide dosage and initial pH of solution on phenol degradation rate were investigated. The maximum mineralization of phenol was achieved at 60°C, 6 g/L $Fe_{78}Si_9B_{13}$, 0.31 mol/L hydrogen peroxide, with an initial pH of 2.5. More than 99% of phenol was completely removed under the optimum conditions within 10 min for a solution containing 1000 mg/L of phenol. Batch experiments for solutions containing phenol concentrations ranging from 50 to 2000 mg/L were investigated under the above conditions and the same excellent degradation rate was obtained. The $Fe_{78}Si_9B_{13}$ showed better catalytic activity than iron powder and Fe^{2+} . Addition of *n*-butannol (hydroxyl radical scavenger) decreased the degradation rate of phenol, which demonstrates that hydroxyl radicals were mainly responsible for the removal of phenol. We demonstrated that phenol may be degraded by hydroxyl radicals decomposed by hydrogen peroxide on the surface of $Fe_{78}Si_9B_{13}$ and illustrated the reaction mechanism for this process. This amorphous alloy exhibited high stability in recycling experiments and showed excellent reuse performance even after continuous operations of 8 cycles.

phenol degradation, iron-based amorphous alloy, heterogeneous catalyst, Fenton reaction

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The expansion in industrial processes has led to an increase in water pollution due to industrial discharges. Most of the pollutants are toxic and resistant to conventional wastewater treatments. Phenol and phenolic compounds are typical pollutants and are classified as teratogenic and carcinogenic compounds [1]. They are discharged into the aquatic environment by industries such as petroleum refineries, petrochemical industries, polymer industries, fiberglass plants, smelting and metallurgical operations, pharmaceutical, paint and dye industries [2–4]. Phenolic compounds are well known for high salinity, acidity, chemical oxygen demand (COD) and low biodegradability [3]. In addition, they have low volatilities and easily form azeotropes and eutectics [5]. All these properties make them difficult to treat. Phenol is lethal to fish at low concentrations (5–25 mg/L) and gives objectionable tastes to drinking water at far lower concentrations [6]. Even a concentration of 1 µg/L can render water unfit for use [3]. The 80/778/EC directive regulates the maximum concentration of phenol in drinking water is 0.5 µg/L [7]. Phenol and phenolic compounds are designated as priority pollutants by the Environmental Protection Agency in the US, and take 11th place in the list of 126 undesirable chemicals [8]. It appears that the problems caused by phenolic-containing wastewater will become worse in the coming decades, therefore, an efficient and environmentalfriendly technology must be found to treat wastewater. Phenol is a common pollutant in industrial discharges and is also believed to be an intermediate product in the oxidation process of higher molecular weight aromatic hydrocarbons. Therefore, it is usually taken as a model compound for wastewater treatment [9].

Current methods for removing phenolics from

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wastewaters include biological degradation, solvent extraction, adsorption and chemical oxidation [3,10–12]. Biological treatment is often the most economical alternative method compared with other processing schemes and it is considered to be environmentally friendly. However, at high concentrations of phenol, this application is restricted because of the inactivation of microorganisms. Microbial degradation usually requires a long time and large land area, so is therefore less flexible in design and operation [13,14].

The solvent extraction method has advantages for treating high concentration wastewater. Its application is based on the high distribution ratio of solute in organic solvents [15]. Through solvent extraction, most phenols can be recovered from wastewater as a by-product, with economic benefit, and the chemical oxygen demand (COD) value of the wastewater can be dramatically reduced [16]. However, the residual phenol concentration in wastewater treated this way barely meets the stringent US Environmental Protection Agency (EPA) requirements (less than 1 mg/L in the wastewater) [17]. In addition, it costs too much to separate solute from the solvent and the loss of solvent will lead to secondary pollution.

The adsorption process is efficient for the removal of organic contaminants and it is usually used only to treat dilute wastewater [18–20]. Activated carbons are the most popular adsorbents due to their excellent adsorption abilities for organic pollutants, especially for phenolic compounds [14]. However, their initial cost is relatively high, the regeneration of saturated carbons is also costly and always results in loss of adsorbents. Moreover, complexing agents are needed to improve its properties in the reaction process [14,21].

Advanced Oxidation Processes (AOPs) are typical chemical methods in which sufficient amounts of active radicals are generated and applied for the degradation of various organic compounds. Recently, a growing number of researchers have paid attention to a new AOP, the catalytic oxidation process (COP). In this process, a catalyst is applied to enhance the oxidation rate and improve the economy of the process [22]. Numerous catalysts, including activated carbon, metal ions, metal oxides and other materials [22-27] have been applied in COPs for oxidizing various hazardous and organic pollutants. In addition, iron and its oxides are the most interesting choices because iron is a widely available and non-toxic element [28]. The classical Fenton oxidation process utilizes the reaction of Fe²⁺ and H_2O_2 to produce hydroxyl radicals, which have a high standard electrode potential (2.80 V) second only to fluorine in its reactivity [29]. The formation of the hydroxyl article can be presented as [29,30]:

$$Fe^{2+} + H_2O_2 \rightarrow Fe^{3+} + OH^- + HO^-, \qquad (1)$$

$$Fe^{3+} + H_2O_2 \rightarrow Fe^{2+} + H^+ + HO_2.$$
 (2)

Compared with other COPs, the Fenton's reaction is easy to operate and maintain. In addition, it provides a cost effective source of hydroxyl radicals [31]. These advantages make it suitable for the treatment of a wide range of hazardous and organic pollutants. Neamtu et al. [31] used the homogenous Fenton process to treat azo dye and their results showed that this method is effective in treating wastewater. However, it is a rather costly process to remove the large volume of sludge after the reaction, requiring a large amount of chemicals and manpower [1,29,32]. In order to overcome this disadvantage, much effort has been put into developing heterogeneous Fenton catalysts to treat wastewater. For example, Fernandez et al. [33] and Sabhi et al. [34] prepared an iron-Nafion film by immobilization of Fe(III) on a Nafion membrane and used it as a photo-Fenton catalyst. Their results showed that the iron-Nafion membrane-based catalyst is effective in removing the organic pollutants from wastewater. However, it should be stressed that the Nafion membranes are too expensive for practical application in wastewater treatment [33,35]. Carbon, supporting iron ions, have been developed and used as a heterogeneous Fenton catalyst [36,37]. Nevertheless, this catalyst exhibited a poor catalytic activity and easily caused the clogging of the instrument due to their small size. Consequently, finding a suitable catalyst for the degradation of phenol and optimizing the reaction conditions are important for wastewater treatment.

The amorphous alloys, sometimes called metallic glasses, are usually obtained by liquid quenching. They have been extensively studied because of their superior mechanical properties and higher corrosion resistance compared with their partner crystals [38]. Among all the amorphous alloys, the iron-based alloys are widely researched for two reasons: first, iron is one of the most plentiful natural resources in the earth's crust, and is therefore a relatively low-cost raw material; second, as a result of the unique combination of their physical, chemical, and mechanical properties, ironbased alloys have high strength and hardness, good corrosion resistance, and excellent soft magnetic properties [39,40]. Iron-based alloys have been produced in bulk compositions so they can be widely applied in industries and the fabrication of many large structural components [38]. In this work, a typical iron-based amorphous alloy, Fe78Si9B13, was chosen as the catalyst for the process of phenol degradation. The effects of reaction temperature, catalyst concentration, hydrogen peroxide concentration, initial pH of solution and initial phenol concentration on the degradation efficiency were systematically investigated and discussed in detail. In addition, the role of hydroxyl radicals in phenol degradation was considered. Finally, the stability and reusability of the Fe78Si9B13 was studied.

1 Materials and methods

1.1 Materials

All reagents used in the experiment were of analytical rea-

gent grade except methanol, which was chromatographic grade and used as a component of the mobile phase for the analysis of phenol. Phenol was purchased from Guangcheng Chemicals Corporation (Tianjin, China) and the other reagents were obtained from Laiyang Chemical Company (Shandong, China). All reagents were used without further purification.

Amorphous $Fe_{78}Si_9B_{13}$ and $Fe_{73.5}Nb_3Cu_1Si_{13.5}B_9$ ribbons, prepared by melt spinning, were supplied by the National Amorphous Nanocrystalline Alloy Engineering Research Center of China. The ribbons were 10 mm in width and $27\pm1 \mu m$ in thickness. They were cut into 5 mm lengths for convenient use in experiments.

1.2 Experimental procedure

The stock solution of phenol (1000 mg/L) was prepared by dissolving a suitable amount of solid reagents in deionized water and storing it in the dark. The initial pH values of the solutions were adjusted with 1 mol/L H_2SO_4 or 1 mol/L NaOH.

To study the activity of the iron-based amorphous alloys for the process of phenol degradation, batch experiments were carried out in 250 mL conical flasks under continuous mechanical stirring in contact with air. A volume of 50 mL phenol aqueous solution, different levels of hydrogen peroxide (30%, w/w) and catalysts were placed into the glass reactor and heated on digital temperature heating units (Xianke Instruments, Shandong).

1.3 Analyses

Samples were periodically withdrawn from the conical flasks and immediately filtered using a plastic syringe filter with nominal pore size of 0.2 μ m to remove suspended particles before analysis. The filtered samples were analyzed by an Elite P230 High Performance Liquid Chromatography (HPLC, Elite Analytical instruments, Dalian, China) installed with a Sinochrom ODS-BP C18 chromatographic column (5 μ m, 4.6 mm×200 mm). A mixture of methanol and de-ionized water (60:40, ν/ν) was used as the mobile phase at a flow rate of 0.75 mL/min. A volume of 5 μ L samples was injected into the sampling system and analyzed with a UV-vis detector (230+, Elite Analytical instruments, Dalian, China) at a wavelength of 270 nm. The detection inferior limit for phenol in this method was 0.02 mg/L and the retention time of phenol was 6.7 min.

2 Results and discussion

2.1 Influence of reaction temperature

Batch experiments were conducted from 15 to 75° C. The degradation efficiency of phenol by different catalysts and reaction temperatures is shown in Figure 1. The removal

rate has been calculated by eq. (3):

Phenol degradation rate (%) =
$$(C_0 - C_t)/C_0$$
, (3)

where C_0 is the initial mass concentration of phenol and C_t is the mass concentration of residual phenol at a given time.

It is known that the kinetic constants (either for radicals production or for iron regeneration) have exponential dependence on reaction temperature (Arrhenius's law) [29], so increasing temperature should accelerate the degradation of phenol in wastewater. However, as shown in the figure, the temperature had a negligible influence on the solution with amorphous Fe₇₈Si₉B₁₃. When the temperature ranged from 15 to 75°C, the phenol removal rates all reached 99%. Initially the solution was colorless but some time later a yellow color appeared. It then changed from orange to brown and finally the color began to disappear. The aromatic intermediates and organic acids that evolved from phenol oxidation were detected during the color change process. Through HPLC analysis, before being degraded to small organic acids, phenol was first oxidized into various aromatic intermediates such as catechol, hydroquinone and benzoquinone, and then decomposed into CO₂ and H₂O. According to Santos et al. [41], hydroquinone and p-benzoquinone are 3 and 2 orders of magnitude more toxic than phenol, respectively, and catechol shows a toxicity value 2-fold that of phenol. Therefore, from an environmental point of view, the disappearance of phenol is still harmful to the environment and it must be oxidized completely into CO₂ and H₂O. At 60 and 75°C, complete removal of phenol and its intermediate products was reached within 50 min. However, when the temperature gradually decreased, a high concentration of toxic intermediates remained in the solution even after 4 h at 45°C. In addition, a relatively high temperature will lead to the decomposition of H₂O₂ and increase the loss of the iron ion [36], which is detrimental to the degradation of phenol. Therefore, the best reaction condition was determined to be 60°C. However, with the amorphous Fe_{73.5}Nb₃-Cu₁Si_{13.5}B₉ alloy as catalyst, the phenol degradation rate was only 79% and 85% at 60 and 75°C, respectively. Moreover, nearly all the removed phenol was converted to toxic intermediates rather than being completely mineralized. A much



Figure 1 Effect of temperature on phenol degradation rate ([phenol]₀ = 1000 mg/L; [catalyst] = 6 g/L; [H₂O₂] = 0.31 mol/L; pH 6; time = 50 min).

longer time was needed for the complete removal of all toxic compounds. Consequently, the amorphous $Fe_{78}S_9B_{13}$ alloy was selected as the catalyst in the following experiments.

2.2 Influence of catalyst amount

The degradation of phenol was investigated in the system of $H_2O_2/Fe_{78}Si_9B_{13}$ under different loads of catalyst. In Figure 2, the results are presented for phenol degradation as a function of catalyst load at various reaction time. It can be seen that, the $Fe_{78}Si_9B_{13}$ shows a significant enhancing effect on the phenol oxidation process, particularly for shorter reaction time. The results indicate that a reaction occurred between catalyst and hydrogen peroxide, in which a new oxidant was produced. We conjectured the new oxidant to be a hydroxyl radical due to that the oxidation potential of hydroxyl radical is higher than hydrogen peroxide.

The increase in catalyst quantity from 2 to 6 g/L accelerated the degradation of phenol after 20 min, giving phenol degradation rates of 79% and 99%, respectively. The phenol removed with 2 g/L catalyst was oxidized into organic intermediates instead of mineralized. The increase of phenol degradation rate with increasing $Fe_{78}Si_9B_{13}$ dosage is related to the increase of catalyst surface area, which enhances the generation of reactive radicals. However, the phenol degradation rate was not enhanced but slightly decreased when the catalyst load was increased to 12 g/L. The lower degree of mineralization may have been due to the excessive iron ions forming iron complexes (iron + organics) [29] and consuming some HO· as follows [36]:

$$HO \cdot + Fe^{2+} \rightarrow Fe^{3+} + OH^{-}.$$
 (4)

As a result, 6 g/L was selected as the optimum concentration in this process and used in the next batches experiment.

2.3 Influence of hydrogen peroxide dosage

100.0

As is well known, the complete degradation of phenol by hydrogen peroxide occurs as shown in eq. (5):



Figure 2 Effect of catalyst dosage on phenol degradation rate ([phenol]₀ = 1000 mg/L; [H₂O₂] = 0.31 mol/L; pH 6; 60°C).

$$C_6H_6O + 14 H_2O_2 \rightarrow 6 CO_2 + 17 H_2O.$$
 (5)

The stoichiometric molar ratio of hydrogen peroxide and phenol is 14:1. Accordingly, 7.5 mmol of hydrogen peroxide is theoretically needed to degrade 50 mL phenol aqueous solution with a concentration of 1000 mg/L. The amount of added hydrogen peroxide varies from 0 to 19.4 mmol. Figure 3 shows that with the addition of hydrogen peroxide the degradation rate of phenol rapidly increased, from 10% to 95% within 10 min. In the presence of hydrogen peroxide, the removal rate of phenol has an obvious increase over 5 min and then the curves become smooth. The increasing dose of hydrogen peroxide within 15.5 mmol resulted in a decrease in the reaction time needed for the complete degradation of the primary intermediates. For example, with the addition of 15.5 mmol hydrogen peroxide, it takes 20 min for complete degradation of phenol, while for 3.8 mmol of hydrogen peroxide, it takes 6 h. However, a further increase in hydrogen peroxide had a detrimental effect on phenol degradation and toxic intermediates were still observed in the reaction solution after 1 h. The negative influence of excess hydrogen peroxide can be explained by reaction (6):

$$HO^{\cdot} + H_2O_2 \rightarrow H_2O + HO_2^{\cdot}.$$
 (6)

Although another radical $(HO_2 \cdot)$ was produced, its standard electrode potential is lower than HO· [36]. In other words, the detrimental effect of excess hydrogen peroxide can be explained as a result of competition between hydrogen peroxide and phenol, as well as its oxidation intermediates for the hydroxyl radicals.

Figure 3 also indicates that hydrogen peroxide is not the only source of oxidants in this process because the solution without hydrogen peroxide still obtained a degradation rate of 15%. In order to evaluate the source of the oxidant, two experiments were carried out using an airtight glass container and an open flask. The phenol concentration was found to be lower by HPLC in the open flask than in the airtight glass container. Therefore, it is consistent with other authors that oxygen in the air proved to be the oxidant of



Figure 3 Effect of H_2O_2 dosage on phenol degradation rate ([phenol]₀ = 1000 mg/L; [catalyst] = 6 g/L; pH 6; 60°C).

phenol [29]. In addition, no phenol degradation intermediates were detected in the airtight condition. This indicates that the reduction of phenol concentration is due to the adsorption by catalyst. The amorphous $Fe_{78}Si_9B_{13}$ alloy has high catalytic activity only in the presence of H_2O_2 .

2.4 Influence of pH

With 1 mol/L H₂SO₄ and/or 1 mol/L NaOH, the effects of pH on the phenol degradation efficiency can be compared. It can be seen from Figure 4 that more than 99% of phenol was removed under acidic conditions and the degradation efficiency was much lower in an alkaline environment. When the initial pH was 2.5, phenol and its oxidation intermediates were completely removed within 10 min but a longer time was needed with a higher initial pH. Figure 4 also demonstrates that under alkaline conditions the activity of the Fe₇₈Si₉B₁₃ was almost negligible and even after 30 min the degradation efficiency remained below 30%. This result can be explained by considering that the Fe78Si9B13 was deactivated in alkaline conditions, and therefore, resulted in reduced leaching of iron ions into the solution. The significant differences in phenol degradation rates under the acidic and alkaline conditions might be caused in two ways. First, hydrogen peroxide is not stable in an alkaline solution and can be quickly decomposed into H₂O and O₂ as shown in eq.(7) [27]:

$$2H_2O_2 \rightarrow 2H_2O + O_2. \tag{7}$$

Second, the lower pH provides more H^+ , which leads to an increasing number of iron ions. As described in eq. (1), the formation of HO· requires a number of iron ions, thus a lower pH resulted in a higher phenol degradation rate. According to all obtained results, the optimum reaction conditions for wastewater treatment are as follows: reaction temperature 60°C, concentration of catalyst and hydrogen peroxide 6 g/L and 0.31 mol/L, respectively, and initial solution pH 2.5. Under these conditions, 10 min was needed for complete removal of 1000 mg/L of phenol in wastewater.

The effect of the initial phenol concentration under the



Figure 4 Effect of initial pH on phenol degradation rate ([phenol]₀ = 1000 mg/L; [H₂O₂] = 0.31 mol/L; [catalyst] = 6 g/L; 60°C).

optimum conditions obtained above was then studied. The initial phenol concentration varied from 50 to 200 mg/L. The effect of this parameter is presented in Figure 5. Similar phenol removal behavior has been found for the concentrations considered, with almost all phenol degraded into their derivatives after 5 min and the intermediates eliminated completely within 10 min.

The degradation of phenol with iron powder and Fe²⁺ was carried out for comparison with Fe78Si9B13. It can be observed from Figure 6 that Fe78Si9B13 is much more efficient than the other two catalysts. All phenol and its derivatives could be completely removed by catalytic oxidation of Fe₇₈Si₉B₁₃. However, the concentration of intermediates was high after the same reaction period when using iron powder and Fe^{2+} as catalyst. The reaction tank was easily blocked by iron powders due to their tiny granule diameters, which can be restrained by $Fe_{78}Si_9B_{13}$. The application of a high concentration of Fe²⁺ will cause environment pollution, and a large amount of manpower and resources was needed for their removal after reaction. The Fe₇₈Si₉B₁₃ could be easily separated from solution simply by applying an external magnetic field due to its magnetic properties [38]. Consequently, Fe₇₈Si₉B₁₃ is a superior catalyst for the removal of organic compounds via the Fenton process.



Figure 5 Effect of initial phenol concentration on phenol degradation rate ($[H_2O_2] = 0.31$ mol/L; [catalyst] = 6 g/L; pH 2.5; 60°C).



Figure 6 The degradation performance of $Fe_{78}Si_9B_{13}$ compared with iron powder and Fe^{2+} ([phenol]₀ = 1000 mg/L; [H₂O₂] = 0.31 mol/L; pH 2.5; 60°C).

2.5 Influence of hydroxyl radical scavenger

In order to confirm the existence of hydroxyl radicals in the phenol degradation process, experiments were carried out in the presence of a hydroxyl radical scavenger, for which n-butanol was selected in this experiment. In comparison, *n*-butanol has a lower toxic value and higher boiling point (117.17°C) than t-butanol (82.5°C), which is the most commonly used hydroxyl radical scavenger in the literature [42,43]. Therefore, the application of *n*-butanol will be more favorable to the environment. The influence of *n*-butanol on the degradation of phenol is shown in Figure 7. It can be seen that the presence of *n*-butanol markedly decreased the reaction rate and removal efficiency for phenol, and the higher the content added to the solution, the poorer the removal became. The results suggest that hydroxyl radicals were mainly responsible for the removal of phenol and its intermediates. Based on these results and the detection of intermediates by HPLC, we proposed the degradation process of phenol to be as follows: the hydrogen peroxide is adsorbed onto the surface of Fe78Si9B13, in order to produce hydroxyl radicals. The hydroxyl radicals first react with phenol in the ortho and para positions to form catechol and hydroquinone, respectively. Further oxidation of the dihydroxylbenzenes then occurs to produce benzoquinones and then the ring opens to form lower molecular weight organic compounds that are ultimately oxidized to CO_2 and H_2O . The breakage of the benzene ring is illustrated in Figure 8.



Figure 7 Effect of *n*-butanol dosage on phenol degradation rate ([phenol]₀ = 1000 mg/L; [H₂O₂] = 0.31 mol/L; pH 2.5; [catalyst] = 6 g/L; 60° C).

2.6 Stability and reusability of the catalyst

Considering the realization of industrial applications, it is necessary to study the stability and reusability of the catalyst in order to achieve the desired environmental and economic benefits. It is known that iron-based amorphous alloys are highly corrosion-resistant [38], which makes them desirable for wastewater treatment. The Fe78Si9B13 separated from the reaction solution was first rinsed with deionized water, then soaked in ethanol for 2 min, and finally dried in a constant temperature drying oven (101-1, Xianke Instruments, Longkou, China) in order to be used in the next batch experiments. The catalyst was reused 8 times under the optimum conditions mentioned above, with no obvious deactivation of the catalyst. The phenol degradation rate was determined after each experiment and the results are shown in Figure 9. It can be seen that the catalytic activity of Fe78Si9B13 remained almost constant after reuse. The fresh and the first cycle catalyst had similar catalytic activities, which were higher than those after further reuse. The reduced degradation efficiency might be explained by the following. First, the leached ions are present during each reuse of the catalyst, which directly results in the loss of the iron ions in the subsequent reactions with further cycles. Second, the formation of deposits on the catalyst surface as well as more iron complexes in the solution prevent the leaching of the iron species. From the liquid chromatogram, it can be seen that the phenol can be completely degraded into H₂O and CO₂ with the fresh and reused catalyst. Consequently, the amorphous Fe₇₈Si₉B₁₃ alloy has been proved to be an appropriate catalyst for the phenol degradation process.

3 Conclusions

Two amorphous alloys were used in the Fenton reaction for wastewater treatment, with the amorphous $Fe_{78}Si_9B_{13}$ alloy showing superior catalytic performance. Oxidation of the catalyst gave rise to highly toxic aromatic intermediates, identified by HPLC analysis, which were further oxidized to CO_2 and H_2O . More than 99% of phenol was completely removed within 10 min at 60°C, 6 g/L $Fe_{78}Si_9B_{13}$, 0.31 mol/L of H_2O_2 and pH 2.5. The results of investigating the



Figure 8 Possible pathway for phenol mineralization.



Figure 9 Effect of repeated cycles of catalyst use on phenol degradation rate $([phenol]_0 = 1000 \text{ mg/L}; [H_2O_2] = 0.31 \text{ mol/L}; pH 2.5; [catalyst] = 6 g/L; 60^{\circ}C).$

influence of a hydroxyl radical scavenger suggest that the hydroxyl radical plays an important role. The generation of hydroxyl radicals was accelerated by the reaction between $Fe_{78}Si_9B_{13}$ and hydrogen peroxide and this enhanced the degradation of phenol. Based on the experiment results, a reasonable mechanism had been proposed to interpret the process for catalytic degradation of phenol. The $Fe_{78}Si_9B_{13}$ catalyst exhibits good stability and reusability, which shows considerable promise for practical applications. In addition, because it shows excellent magnetic properties, the $Fe_{78}Si_9B_{13}$ catalyst can be readily separated from effluents by applying an external magnetic field.

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