available at www.sciencedirect.com journal homepage: www.elsevier.com/locate/chnjc

Article

CoFe/SBA-15 catalyst coupled with peroxymonosulfate for heterogeneous catalytic degradation of rhodamine B in water

Longxing Hu*, Fan Yang, Lianpei Zou, Hang Yuan, Xing Hu

School of Environmental and Chemical Engineering, Shanghai University, Shanghai 2000444, China

ARTICLE INFO

Article history:

Received 18 May 2015

Accepted 17 June 2015

Published 20 October 2015

Keywords:

Cobalt

Iron

SBA-15

Peroxymonosulphate

Rhodamine B degradation

Advanced oxidation technologies

Sulfate radical

ABSTRACT

CoFe/SBA-15 catalysts were prepared by simultaneous incipient wetness impregnation using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ as the precursors and SBA-15 as the support. The catalysts were used to activate generation of sulfate radicals from peroxymonosulfate (PMS) for rhodamine B (RhB) dye degradation in aqueous solutions. The catalyst was characterized using X-ray diffraction, N_2 adsorption-desorption, scanning electron microscopy and energy-dispersive X-ray spectroscopy, transmission electron microscopy, and vibrating sample magnetometry. The effects of the Co and Fe loadings and calcination temperature on the catalytic performance, catalyst reusability, and kinetics and mechanism of catalytic oxidative degradation of RhB in the presence of CoFe/SBA-15 and PMS were investigated. The results show that the predominant Co-Fe oxide loaded on the support was the composite CoFe_2O_4 , which provided the active catalytic sites, and was present in the SBA-15 matrix. The surface area, pore volume, and mean pore diameter of 10Co9.5Fe/SBA-15-700 were $506.1 \text{ m}^2/\text{g}$, $0.669 \text{ cm}^3/\text{g}$, and 7.4 nm , respectively, lower than those of SBA-15. 10Co9.5Fe/SBA-15-700 consisted of rod-like aggregates with diameters greater than $0.25 \mu\text{m}$. It had a magnetic intensity of 8.3 emu/g ; therefore, magnetic separation was feasible. 10Co9.5Fe/SBA-15-700 showed good catalytic activity and stability, with a RhB degradation rate higher than 96% and Co leaching lower than $32.4 \mu\text{g/L}$. The catalytic oxidative degradation of RhB in the presence of FeCo/SBA-15 and PMS obeyed first-order kinetics, and the degradation rate increased with increasing CoFe/SBA-15 and PMS dosages and with decreasing initial reactant concentrations. Quenching tests showed that sulfate radicals played a dominant role in RhB catalysis. CoFe/SBA-15 maintained high catalytic activity and good stability during 10 recycling runs, with a RhB degradation rate greater than 84%, Co and Fe leaching for each run lower than 72.1 and $35 \mu\text{g/L}$, respectively. CoFe/SBA-15 is an efficient catalyst for PMS oxidation, and has potential applications in the removal of refractory organics such as RhB in water.

© 2015, Dalian Institute of Chemical Physics, Chinese Academy of Sciences.

Published by Elsevier B.V. All rights reserved.

1. Introduction

Advanced oxidation techniques are innovative water and wastewater treatment methods based on the in situ generation of highly reactive radicals such as $\text{OH}^\bullet$, $\text{O}_2^{\bullet-}$, $\text{OOH}^\bullet$, and $\text{SO}_4^{\bullet-}$ (sulfate radical). They are used for degradation and mineraliza-

tion of refractory organic pollutants [1–5]. In the last decade, sulfate-radical-based advanced oxidation techniques have received much attention for environmental applications, because at neutral pH, $\text{SO}_4^{\bullet-}$ is a powerful and selective oxidant for the decomposition of organic pollutants, and its use avoids some of the disadvantages of conventional Fenton processes [3,6,7].

* Corresponding author. Tel/Fax: +86-21-66137771; E-mail: hulxhbb@shu.edu.cn

This work was supported by Program for Innovative Research Team in University (IRT 13078).

DOI: 10.1016/S1872-2067(15)60939-1 | <http://www.sciencedirect.com/science/journal/18722067> | Chin. J. Catal., Vol. 36, No. 10, October 2015

Sulfate generation using a combination of transition-metal ions with oxone or peroxymonosulfate (PMS) is a highly efficient method for the degradation of organic pollutants [3,7]; Co ions are the best activator [7]. However, the detrimental impact of Co dissolved in water on human health is a serious concern, therefore it is important to develop heterogeneous Co catalysts.

Environmental applications of various heterogeneous Co-based catalysts coupled with oxone or PMS have been investigated, i.e., unsupported Co oxides such as Co_3O_4 [5,8,9], unsupported Co-based mixed oxide composites such as Fe-Co mixed oxide nanocomposites [10–12], supported Co catalysts, including oxide-supported Co catalysts such as TiO_2 -, Al_2O_3 -, SiO_2 -, MgO -, ZnO -, and ZrO_2 -loaded Co catalysts [13–18], carbon-supported Co catalysts such as Co/activated carbon [19], Co/carbon aerogel [20], Co/carbon xerogel [21], and Co_3O_4 / or CoFe_2O_4 /graphene oxide [22–24], Co-exchanged zeolites [25,26], Co-exchanged resins [26], Co catalysts supported on industrial solid wastes such as Co/red mud and Co/fly ash [27], and mesoporous-material-supported Co catalysts such as Co/SBA-15 [28–30], Co/mesoporous MnO_2 [31], and Co/MCM-41 [32]. Heterogeneous Co catalysts must have (1) high catalytic activity, reflected by the degradation efficiency and rate, and stability, represented by Co leaching in water and the recycling performance; and (2) convenient recovery of the catalyst after use for water and wastewater treatment [10]. The development of improved heterogeneous Co catalysts and the fabrication of novel heterogeneous Co catalysts for pollution control are of great importance.

The porous material SBA-15 is a mesoporous silica molecular sieve with a highly ordered structure, large pore size, and high surface area [33,34]; these properties favor the loading and dispersion of catalytic active components and give good adsorption capabilities, thereby increasing the catalytic activity and stability. Previous investigations [28–30] showed that Co-supported SBA-15 coupled with PMS was effective in phenol and rhodamine B (RhB) degradation in water, and is stable. However, the use of Co-supported SBA-15 catalysts that are potentially excellent heterogeneous catalysts for oxone or PMS activation in the degradation of refractory organic pollutants need to be investigated further.

RhB is an important water-soluble xanthene organic dye. It is widely used in various industries, resulting in dye effluents. RhB in water is a threat to human health and the environment. The complex structure and stability of RhB make it resistant to biodegradation and photodegradation. The principal techniques available for removing RhB from water are adsorption [35], photocatalytic oxidation [36], the Fenton process [37], ultrasonic degradation [38], ozonation [39], and electrochemical oxidation [40]. Adsorption is convenient to operate and gives a high removal efficiency, but it only transfers the pollutants from the liquid phase to the solid phase, causing secondary pollution. Other techniques need special equipment or facilities, or have high energy consumption, leading to high capital and operating costs. The Fenton process is rapid and inexpensive, but it has several significant drawbacks such as needing an acidic pH (pH 2–4) and a high Fe dosage, which produces a large amount of Fe sludge, and the total organic carbon remov-

al is less than 60%.

In preliminary tests, we investigated the removal of RhB in aqueous solutions using Co/SBA-15-PMS or Fe/SBA-15-PMS systems. We found that Co/SBA-15 had high catalytic activity but could not be easily recovered because of its fine particle size. Degradation of RhB using Fe/SBA-15 was much slower than that with Co/SBA-15; the apparent reaction rate constant for Fe/SBA-15 was one-tenth that of CoFe/SBA-15. CoFe/SBA-15 was therefore expected to give better performance in the activation of PMS in RhB degradation, because it can maintain a high catalytic activity because of the presence of Co species, and provide different catalytic active sites and magnetism, enabling catalyst separation and recovery, because of the presence of Fe species. In this paper, SBA-15-supported Co and Fe was prepared and used to activate PMS to generate sulfate radicals for RhB degradation in aqueous solutions. The effects of the Co and Fe loadings and calcination temperature on the catalytic performance, and those of the CoFe/SBA-15 and PMS dosages and initial reactant concentrations on RhB degradation were investigated. A RhB degradation mechanism was proposed and the recycling performance of the CoFe/SBA-15 was investigated.

2. Experimental

2.1. Preparation of SBA-15 and CoFe/SBA-15

SBA-15 was prepared according to the procedure described by Zhao et al. [33]. Pluronic P123 triblock copolymer ($\text{EO}_{20}\text{-PO}_{70}\text{-EO}_{20}$, Aldrich) and tetraethyl orthosilicate (TEOS, Aldrich) were used as the templating agent and silica source, respectively. In a typical synthesis, pluronic P123 (4.0 g) was dissolved in double-distilled water (30 g) and 2 mol/L HCl (120 g, AR, Sinopharm Chemical Reagent Co., Ltd. (SCRC)) solution with stirring at 35 °C. TEOS (8.50 g) was added with stirring at 35 °C for 20 h. The mixture was aged at 80 °C overnight without stirring. The solid product was recovered, washed, and air dried at room temperature. The dried solid was calcined in air at 500 °C for 6 h. The heating rate was 1 °C/min.

CoFe/SBA-15 catalysts were prepared via one-step incipient wetness impregnation using $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ (AR, SCRC) and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ (AR, SCRC) as the precursors, and SBA-15 as the support, with Co loadings of 3 wt%, 7 wt%, 10 wt%, and 12 wt%, and Fe loadings of 2.9 wt%, 4.8 wt%, 6.7 wt%, 9.5 wt%, 11.4 wt%, and 19 wt%. The appropriate amounts of $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were dissolved in distilled water under vigorous stirring. The suspension was stirred for 24 h and then mixed with SBA-15. The impregnated solids were dried at 60 °C for 10 h, and then calcined in air at 400–700 °C for 5 h. The heating rate was 10 °C/min. The resulting catalysts were denoted by *m*Co*n*Fe/SBA-15-*o*, where *m*, *n*, and *o* represent a Co loading of *m* wt%, Fe loading of *n* wt%, and the calcination temperature (°C), respectively.

2.2. Characterization of prepared CoFe/SBA-15

X-ray diffraction (XRD) patterns of the prepared samples

were obtained using a Rigaku D/Max-2200X powder X-ray diffractometer with a Cu $K\alpha$ radiation ($\lambda = 0.154056$ nm) at 40 kV and 40 mA. Small-angle data were collected from 0.5° to 5.0° (2θ) at a scanning speed of $0.5^\circ/\text{min}$; wide-angle data were collected from 10° to 80° (2θ) at a scanning speed of $5^\circ/\text{min}$. N_2 adsorption-desorption isotherms were measured using a Micromeritics Tristar 3000 instrument at -196°C . The specific surface areas were evaluated using the Brunauer-Emmett-Teller (BET) method in the p/p_0 range 0.02–0.20. The pore size distributions were calculated using the Barrett-Joyner-Halenda method, based on the adsorption branch. The total pore volumes were determined from the data at $p/p_0 = 0.99$. The surface morphologies of the samples were examined using scanning electron microscopy (JSM-6700F) with energy-dispersive X-ray spectroscopy (EDS). The internal structures of the samples were examined using high-resolution transmission electron microscopy (HR-TEM; JEM-2010F, JEOL, with a field-emission gun, 200 kV). The room-temperature magnetic properties of the samples were investigated using vibrating sample magnetometry (VSM; Lake Shore 7407) at magnetic fields up to 20 kOe.

2.3. Catalytic oxidative degradation (catalytic reaction mode)

RhB catalytic oxidative degradation tests were performed at 25°C in 1000 mL glass reactors with 500 mL of magnetically stirred 5–25 mg/L RhB solution. The initial solution pH was not adjusted. CoFe/SBA-15 was added to the RhB solutions at dosages ranging from 0.05 to 0.2 g/L, and the suspensions were stirred for 5 h to achieve RhB adsorption-desorption equilibrium. The RhB concentrations at adsorption-desorption equilibrium were taken as the initial concentrations (C_0) for the RhB catalytic oxidative degradation. A given amount of PMS (KHSO_5 , the active component of oxone ($2\text{KHSO}_5 \cdot \text{KHSO}_4 \cdot \text{K}_2\text{SO}_4$), Shanghai Future Chemical Technology Co., Ltd.) in the PMS/RhB molar ratio range 10:1–60:1 was added to the reactor to initiate the reaction. The reactor was covered to avoid volatilization. At fixed intervals, suspension samples (7 mL) were removed using a syringe and quenched with excess sodium nitrite to stop the reaction. The RhB concentrations in the aqueous solutions were determined using ultraviolet-visible (UV-vis) spectrophotometry (UV-5300PC) at 552 nm. The Co concentrations in the solutions were measured by the nitroso-R-salt spectrophotometric method using a 722E visible spectrophotometer at 425 nm. The Fe concentrations in the solutions were measured using inductively coupled plasma-atomic emission spectroscopy (Prodigy).

2.4. RhB removal in presence of CoFe/SBA-15 and PMS (combined adsorption and catalytic reaction mode)

In this investigation, the performances of CoFe/SBA-15 catalysts were investigated, in terms of the catalytic activity and stability, based on RhB removal, and Co and Fe leaching, respectively, in aqueous solutions. Co or Fe leaching was represented by the leaching concentration (dissolved Co or Fe concentration in solution) and leaching percentage (percentage

loss of Co or Fe into the solution). For the combined adsorption and catalytic reaction tests, CoFe/SBA-15 was added to the RhB solution, immediately followed by addition of PMS to initiate the reaction. The other steps were the same as those described above. All RhB removal tests were conducted using this operating mode, apart from the catalytic oxidative degradation tests. UV-vis spectra were obtained at different reaction times, in the scanning range 250–650 nm. For the CoFe/SBA-15 recycling tests, several parallel reactions were performed in every run up to the last one to ensure that sufficient material was available for the next run. The tests were conducted in duplicate and the experimental errors were below 3%.

3. Results and discussion

3.1. Characterization of SBA-15 and CoFe/SBA-15

3.1.1. XRD

The small-angle XRD patterns of SBA-15 and $10\text{Co}9.5\text{Fe/SBA-15-700}$ are shown in Fig. 1. SBA-15 has an intense major diffraction peak corresponding to the (100) reflection and two additional peaks at higher degrees, corresponding to (110) and (200) reflections, respectively, indicating significant long-range order of the p6mm hexagonal symmetry. The diffraction peaks indexed to the (100), (110), and (200) reflections are also observed for $10\text{Co}9.5\text{Fe/SBA-15-700}$, but the intensities are appreciably lower. This can be attributed to a decrease in the electron density contrast as a result of Co and Fe incorporation [41], implying that the supported Co and Fe species entered the SBA-15 channels.

Figure 2 shows the wide-angle XRD patterns of $m\text{CoFe/SBA-15-}o$ with various Co and Fe loadings and calcination temperatures. No distinct diffraction peaks were observed in the $3\text{Co}2.9\text{Fe/SBA-15-700}$ (Fig. 2(a)); this implies that the Co and Fe species were highly dispersed on the SBA-15, preventing the formation of large crystallites. The reflection intensities increased significantly with increasing Co and Fe loadings, as a result of enhanced Co and Fe aggregation on the SBA-15 surface. However, calcination temperatures in the range 400 – 700°C had little effect on the reflection intensities (Fig. 2(b)). The characteristic diffraction peaks of CoFe_2O_4 in Fig. 2 suggest that

Fig. 1. Small-angle XRD patterns of SBA-15 (1) and $10\text{Co}9.5\text{Fe/SBA-15-700}$ (2).

Fig. 2. Wide-angle XRD patterns of *mConFe*/SBA-15-700 with different Co and Fe loadings (a) and 10Co9.5Fe/SBA-15 calcined at various temperatures (b).

Co and Fe were present mainly in the form of a CoFe_2O_4 composite in all the calcined samples. It has been reported that among the various linkages in CoFe_2O_4 , i.e., Co–Co, Fe–Fe, and Co–Fe, the Co–Fe interaction is the strongest [42]. The formation of abundant CoFe_2O_4 species can therefore suppress Co leaching.

Table 1

Textural parameters of SBA-15 and 10Co9.5Fe/SBA-15-700.

Sample	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore diameter* (nm)
SBA-15	858.0	1.083	8.3
10Co9.5Fe/SBA-15-700	506.1	0.669	7.4

* calculated from the adsorption branch of the isotherm.

3.1.2. N_2 adsorption-desorption

The N_2 adsorption-desorption isotherms of SBA-15 and 10Co9.5Fe/SBA-15-700 are shown in Fig. 3. Both samples had the type IV isotherm with an H1-type hysteresis loop resulting from capillary condensation of N_2 in the mesopores; this is characteristic of mesoporous materials with cylindrical mesostructures. The isotherm of SBA-15 displayed a sharp jump at $p/p_0 = 0.6\text{--}0.8$, indicating that the sample had a typical mesostructure, with a uniform pore size distribution. However, the isotherm of 10Co9.5Fe/SBA-15-700 showed a sharp jump at $p/p_0 = 0.4\text{--}0.8$, i.e., lower than that for SBA-15, indicating that the pore size of the SBA-15 support decreased after loading with Co and Fe species, and the supported species entered the SBA-15 channels.

The textural parameters of 10Co9.5Fe/SBA-15-700 are listed in Table 1. They show that the introduction of Co and Fe led to a 41% decrease in the specific surface area, 38% decrease in the pore volume, and 11% decrease in the pore diameter. This is because the Co-Fe composite formed by calcination occupied SBA-15 pore spaces. As shown in the inset in Fig. 3, SBA-15 and 10Co9.5Fe/SBA-15-700 both had a narrow pore size distribution, suggesting that the pore size distribution of SBA-15 was still uniform after Co and Fe species loading.

3.1.3. SEM and EDS

Figure 4 shows SEM images of SBA-15 and 10Co9.5Fe/SBA-15-700. The images show that the samples consist of rod-like aggregates with diameters greater than $0.25\text{ }\mu\text{m}$. A comparison of Figs. 4(b) and (d) shows a larger number of small particles attached to the surface of 10Co9.5Fe/SBA-15-700, indicating that some Co-Fe composites agglomerated on the external surface of the catalyst, forming larger particles of diameter up to 100 nm . The elements in 10Co9.5Fe/SBA-15-

Fig. 3. N_2 adsorption-desorption isotherms (a) and pore diameter distributions (b) for SBA-15 and 10Co9.5Fe/SBA-15-700.

Fig. 4. SEM images of SBA-15 (a, b) and 10Co9.5Fe/SBA-15-700 (c, d), and EDS analysis of 10Co9.5Fe/SBA-15-700 (e).

700 were determined using EDS; the results are shown in Fig. 4(e). 10Co9.5Fe/SBA-15-700 contains Co, Fe, Si, and O; Co and Fe account for 9.33 wt% and 8.93 wt%, respectively, consistent with their theoretical values.

3.1.4. TEM

The TEM images of 10Co9.5Fe/SBA-15-700 in Fig. 5 show well-ordered hexagonal mesoporous channels. It can be seen from Fig. 5(a) that the formed CoFe_2O_4 nanoparticles were evenly dispersed in the SBA-15 channels, indicating that the nanoparticles had high crystallinity and phase purity, and that the supported catalyst retained the two-dimensional p6mm hexagonal mesostructure [33] after the introduction of CoFe_2O_4 . The average thickness of the pore wall and the pore diameter were estimated to be around 4.95 and 6.6 nm, respectively, based on the specific scale shown in Fig. 5(b); these values are consistent with those obtained from BET surface area analysis and the XRD results.

3.1.5. VSM

The magnetization curve for 10Co9.5Fe/SBA-15-700 is

Fig. 5. TEM images (a) and HRTEM images (b) of 10Co9.5Fe/SBA-15-700.

shown in Fig. 6. The catalyst is magnetic, with a maximum magnetic intensity of 8.3 emu/g; it can therefore be conveniently separated from water using a magnet. The convergence of the catalyst under the influence of an external magnet indicated the feasibility of catalyst reuse in practical applications. Among the Co-Fe oxides, i.e., Co_3O_4 , CoFe_2O_4 , and Fe_2O_3 , that can be formed by calcination in the preparation of CoFe/SBA-15, only CoFe_2O_4 has magnetic properties, confirming that the mixed oxide CoFe_2O_4 was the major Co-Fe species on SBA-15 after calcination; this is consistent with the XRD results.

3.2. Effects of CoFe/SBA-15 preparation conditions on catalytic performance

3.2.1. Calcination temperature

Figure 7 shows the effect of calcination temperature on the catalytic performance, i.e., RhB removal and Co leaching in the presence of CoFe/SBA-15 and PMS. The results show that the effect of the calcination temperature on RhB removal is negligible, with RhB removal always being greater than 98%; howev-

Fig. 6. Magnetization curve of 10Co9.5Fe/SBA-15-700.

Fig. 7. Effects of calcination temperature on RhB removal and Co leaching. Reaction conditions: C_{RhB} 5.0 mg/L, 10Co9.5Fe/SBA-15 0.10 g/L, PMS/RhB molar ratio 20:1, 25 °C, 2 h, no solution pH adjustment.

er, the effect on Co leaching is significant. In general, a higher calcination temperature suppressed Co leaching. The maximum Co leaching concentration, i.e., 297.8 μg/L (3.5%), and the minimum Co leaching concentration, 32.4 μg/L (0.4%), were achieved at 400 and 700 °C, respectively, indicating that the calcination temperature significantly affected the CoFe/SBA-15 stability. It can be inferred that Co and Fe species were attached to the support more firmly after calcination at 700 °C.

3.2.2. Co and Fe loadings

Figure 8 shows the effects of Co and Fe loadings on RhB removal and Co leaching for CoFe/SBA-15-700. As the results shown, the effects of the Co and Fe loadings on RhB removal were insignificant; the RhB removal exceeded 96%. The effects on Co leaching were also negligible, with Co leaching ranging from 20 to 60 μg/L. At 3 wt% Co loading, the Co leaching concentration and percentage were 23.3 μg/L and 0.82%, respectively, and at 10 wt% Co loading, the Co leaching concentration and percentage were 32.4 μg/L and 0.39%, respectively. Although the Co leaching concentrations are similar in the above cases, the Co leaching percentage in the latter case is only half that in the former. 10Co9.5Fe/SBA-15-700 displayed the highest catalytic activity and negligible Co leaching, and is therefore considered to be the best catalyst.

3.3. Preliminary tests

As a preliminary test, the changes in RhB concentration in aqueous solution with time under different operating modes

Fig. 8. Effects of Co and Fe loadings on RhB removal and Co leaching. Reaction conditions: C_{RhB} 5.0 mg/L, CoFe/SBA-15-700 0.10 g/L, PMS/RhB molar ratio 20:1, 25 °C, 2 h, no solution pH adjustment.

were investigated: simple adsorption by 10Co9.5Fe/SBA-15-700, chemical oxidation with PMS alone, and a combination; the results are shown in Fig. 9. The results show that the contribution of chemical oxidation by PMS to RhB removal is negligible. Simple adsorption by 10Co9.5Fe/SBA-15-700 can remove approximately 45% of RhB in solution, and approximately 98% RhB removal can be achieved in 2 h in the presence of 10Co9.5Fe/SBA-15-700 and PMS, suggesting that an important chemical reaction occurs in the system consisting of CoFe/SBA-15, PMS, and RhB in solution, i.e., the activation of PMS by 10Co9.5Fe/SBA-15-700 and subsequent generation of sulfate radicals, leading to RhB degradation in aqueous solutions.

Fig. 9. Removal of RhB in aqueous solution under three operational modes. Reaction conditions: C_{RhB} 5.0 mg/L, CoFe/SBA-15-700 0.10 g/L, PMS/RhB molar ratio 20:1, 25 °C, 2 h, no solution pH adjustment.

3.4. Kinetics of catalytic oxidative degradation of RhB in the presence of CoFe/SBA-15 and PMS

Evaluation of the catalytic activity of CoFe/SBA-15 should be based on the catalytic oxidative degradation of RhB rather than on RhB adsorption on CoFe/SBA-15. It is necessary to investigate the RhB degradation kinetics to understand RhB degradation in the presence of CoFe/SBA-15 and PMS. Accordingly, three groups of tests, described below, were conducted in catalytic reduction mode, using 10Co9.5Fe/SBA-15-700 as a representative CoFe/SBA-15 catalyst.

3.4.1. Effect of 10Co9.5Fe/SBA-15-700 dosage

10Co9.5Fe/SBA-15-700 was used as the catalyst to activate the PMS oxidant to produce active sulfate radicals, with RhB as the target compound for radical attack, in the heterogeneous system 10Co9.5Fe/SBA-15-700-PMS-RhB in catalytic reaction mode. The generation of sulfate radicals is important in RhB degradation and is significantly affected by the catalyst and oxidant. The effect of the 10Co9.5Fe/SBA-15-700 dosage on the degradation kinetics was investigated first; the RhB degradation rate constant k_1 and Co leaching rates at different 10Co9.5Fe/SBA-15-700 dosages in the presence of PMS are shown in Fig. 10. The inset in Fig. 10(a) shows the kinetic curves of RhB degradation; these illustrate that RhB degradation corresponds well to the first-order kinetic model $\ln(C/C_0) = -k_1t$, where C and C_0 are the RhB concentrations at time t and $t = 0$, respectively. Figure 10(a) shows that the rate constant k_1 jumps, increasing from approximately 0.017 to 0.032 min⁻¹, as the catalyst loading increases from 0.05 to 0.10 g/L. At catalyst loadings above 0.10 g/L, k_1 is constant, at approximately 0.032 min⁻¹. A higher catalyst dosage increases the number of adsorption sites and provides more active sites for activating sulfate radical generation by PMS, and therefore leads to a significant enhancement in the oxidative degradation rate. In addition, it has been reported that for degradation in the presence of PMS alone at a PMS/RhB molar ratio of 20:1, a decrease in the RhB concentration of less than 15% occurred in 120 min, confirming the critical role of the CoFe/SBA-15 catalyst in RhB degradation [30].

Co leaching rates at representative catalyst dosages in the

presence of PMS and RhB are shown in Fig. 10(b); Co leaching was negligible in ordinary RhB aqueous solution. As shown in Fig. 10(b), Co leaching increased significantly from less than 32.4 μg/L (0.39%) to 120.9 μg/L (0.72%) as the 10Co9.5Fe/SBA-15-700 dosage increased from 0.1 to 0.2 g/L; at a 10Co9.5Fe/SBA-15-700 loading greater than 0.10 g/L, the degradation rate constant k_1 was maximum and approximately constant, i.e., 0.032 min⁻¹, indicating the fastest RhB degradation rate, fastest generation rate of organic acid intermediates, and the most acidic solution, which is favorable for Co leaching. Moreover, loading of a larger number of Co species in the acidic solution would lead to more Co leaching in the solution. Melero et al. [43] investigated the catalytic wet peroxidation of phenolic aqueous solutions with Fe₂O₃/SBA-15, and found that a significant decrease in the solution pH resulted in higher Fe leaching; this was associated with the formation of organic carboxylic acids as the main byproducts of the partial oxidation of phenolic compounds. These observations are similar to ours. It was also reported that RhB degradation increased from 39% to 72% in 60 min in a homogeneous Co(II)-PMS system as the Co ion concentration increased from 50 to 200 μg/L, while keeping the RhB concentration and PMS/RhB molar ratio at 5.0 mg/L and 20:1, respectively [30]. In comparison, RhB degradation was much higher in our heterogeneous system, with Co leaching into solution, showing a heterogeneous reaction mechanism rather than a homogeneous one.

3.4.2. Effect of PMS dosage

Figure 11 shows the catalytic oxidative degradation rate constant k_1 and Co leaching rates at different PMS dosages in the presence of 10Co9.5Fe/SBA-15-700. The inset in Fig. 11(a) shows the kinetic curves for RhB degradation; they illustrate that RhB degradation followed the first-order kinetic model well. The initial RhB concentration of the solution was as low as 5.0 mg/L, to simulate dilute effluent, therefore the RhB degradation rate was related to the instantaneous concentration of RhB, and was one of the rate-limiting factors. Figure 11(a) shows that the kinetic rate constant increased with increasing PMS dosage, with k_1 equaling 0.042 min⁻¹ at a PMS/RhB molar ratio of 60:1. Because PMS is the origin of the reactive sulfate radicals, increasing the PMS dosage promotes generation of

Fig. 10. Performances of catalyst at various 10Co9.5Fe/SBA-15-700 dosages in the presence of PMS and RhB. (a) RhB degradation kinetics; (b) Co leaching. Reaction conditions: C_{RhB} 5.0 mg/L, PMS/RhB molar ratio 20:1, 25 °C, 2 h, no solution pH adjustment.

Fig. 11. Performances of 10Co9.5Fe/SBA-15-700 catalyst at various PMS dosages in the presence of RhB. (a) RhB degradation kinetics; (b) Co leaching. Reaction conditions: C_{RhB} 5.0 mg/L, 10Co9.5Fe/SBA-15-700 0.10 g/L, 25 °C, 2 h, no solution pH adjustment.

sulfate radicals, resulting in a faster degradation rate. It has been reported that further increasing the PMS dosage leads to lower degradation rates for organic materials in systems consisting of a Co-based catalyst and PMS because of self-quenching of sulfate radicals by PMS, as shown in equation (3) [44].

However, significant self-quenching resulting from a higher PMS dosage was not observed in this investigation, probably because the proportions of the CoFe/SBA-15 catalyst, PMS oxidant, and RhB target compound were appropriate.

As observed in Fig. 11(b), the Co leaching concentration and percentage increased from 32.4 μg/L and 0.39% to 58.2 μg/L and 0.70%, respectively. The increased Co leaching can be ascribed to the increased acidity of the solution as a result of the increased acidic oxidant (oxone) dosage and generation of acidic intermediates during degradation.

3.4.3. Effect of different initial reactant concentrations

Figure 12 shows the kinetic rate constants k_1 and Co leaching rates at different initial reactant (RhB and PMS) concentrations with a fixed PMS/RhB molar ratio of 20:1 in the presence of 10Co9.5Fe/SBA-15-700. The inset in Fig. 12(a) shows the

kinetic curves for RhB degradation, and these indicate that RhB degradation still obeyed the first-order kinetic model with respect to the substrate, i.e., RhB. Figure 12(a) shows that the kinetic rate constant declined from 0.032 to 0.010 min⁻¹ with increasing initial RhB concentration from 5 to 25 mg/L coupled with an increase in the initial PMS concentration from 32 to 159 mg/L. The increases in the initial RhB and PMS concentrations result in the production of larger amounts of intermediates and carbonaceous deposits on the catalyst during RhB degradation, leading to active site blockage. This is why the degradation rate decreased with increasing initial reactant concentrations. Ramirez et al. [45] investigated azo-orange II degradation via a heterogeneous Fenton-like reaction, using Fe/carbon catalysts. They attributed the observed Fe/active carbon catalyst deactivation to Fe complexation with oxalic acid and/or to active site blockage by polymeric deposits. This explanation is similar to ours. It was observed that the initial pH of the suspension of CoFe/SBA-15, PMS, and RhB decreased from 5.2 to 3.8 when the initial RhB concentration increased from 5 to 25 mg/L while keeping the PMS/RhB molar ratio at 20:1, because PMS and RhB are both acidic compounds. At low pH values, the formation of Co-OH complexes on the Co cata-

Fig. 12. Performances of 10Co9.5Fe/SBA-15-700 catalyst at various reactants (PMS and RhB) concentrations. (a) RhB degradation kinetics; (b) Co leaching. Reaction conditions: PMS/RhB molar ratio 20:1, 10Co9.5Fe/SBA-15-700 0.10 g/L, 25 °C, 2 h, no solution pH adjustment.

lyst surface decreased, which inhibited heterogeneous activation of PMS and decreased the RhB degradation rate [18]. Su et al. [12] investigated the influence of pH on RhB degradation in $\text{Co}_x\text{Fe}_{3-x}\text{O}_4/\text{oxone}$ systems, and found that the degradation rate was low under strongly acidic and alkaline conditions. Anipsitakis et al. [46] reported similar results. These results are similar to ours. The decrease in the solution pH as a result of increasing the initial reactant concentrations is therefore also responsible for the reduced RhB degradation rate in the CoFe/SBA-15-PMS system.

Figure 12(b) shows that Co leaching increased with increasing initial reactant concentrations. As explained above, higher concentrations of the reactants (PMS and RhB) increase the suspension acidity, which promotes dissolution of supported metallic species such as Co ions in aqueous solution.

Table 2 lists most of the reported rate constants for the first-order kinetics of organic degradation in the presence of PMS and Co-loaded catalysts with different supports. As shown in Table 2, in various cases, CoFe/SBA-15 coupled with PMS for degradation of the non-biodegradable organic dye RhB gave high degradation rate constants. It is also worth noting that the catalytic activity of CoFe/SBA-15 is lower than that of Co/SBA-15 under similar reaction conditions: RhB concentration 5.0 mg/L, Co/SBA-15 or 10Co9.5Fe/SBA-15-700 dosage 0.10 g/L, PMS/RhB molar ratio 60:1, 25 °C, 2 h, and no solution pH adjustment. This phenomenon can be attributed to the different catalysts having different degradation mechanisms.

3.5. Mechanism of RhB removal from aqueous solutions in presence of CoFe/SBA-15 and PMS

3.5.1. UV-vis spectroscopy

The pathway of RhB degradation was explored by examining the UV-vis spectra of RhB degradation in the presence of a catalyst and oxidant. Figure 13 shows the temporal evolution of spectral changes during RhB degradation in the presence of 10Co9.5Fe/SBA-15-700 and PMS. It is generally accepted that RhB degradation occurs via two competitive processes: continuous N-de-ethylation, and destruction of anthracene rings [47,48]. It shows that there is no significant blue shift of the maximum adsorption peak at 552 nm and only a gradual decrease in the intensity, and no new bands are formed. These results indicate that the major RhB degradation pathway is the destruction of anthracene rings, and there is no complex formation among CoFe/SBA-15, PMS, and RhB. It can therefore be

Fig. 13. UV-vis spectra of RhB degradation on 10Co9.5Fe/SBA-15-700. Reaction conditions: C_{RhB} 5.0 mg/L, 10Co9.5Fe/SBA-15-700 dosage 0.10 g/L, PMS/RhB molar ratio 20:1, 25 °C, 2 h, no solution pH adjustment.

concluded that the $\text{SO}_4^{\bullet-}$ radicals generated by PMS activation by 10Co9.5Fe/SBA-15-700 preferentially attack the aromatic hydrocarbon rings, and decompose RhB molecules to small-molecule organics in 60 min. The reduction in the intensity of the absorbance peak in the initial degradation phase does not exclude RhB adsorption on the 10Co9.5Fe/SBA-15-700 catalyst.

Yang et al. [10] developed an efficient and environmentally benign Fe-Co mixed oxide nanocatalyst for heterogeneous activation of PMS to generate sulfate radicals for the decomposition of 2,4-dichlorophenol, and found that a CoFe_2O_4 catalyst had the following physicochemical properties. (1) The Co species in CoFe_2O_4 are present as Co(II), which avoids the detrimental effect of Co(III) on PMS activation. (2) CoFe_2O_4 suppresses Co leaching because of strong Fe–Co interactions, i.e., Fe–Co linkages. (3) CoFe_2O_4 is easy to recovery because of its ferromagnetic nature. (4) The conjunction of Co with Fe increases the number of hydroxyl groups on the catalyst surface, and this facilitates the formation of Co(II)–OH complexes, which are vital to heterogeneous PMS activation. In this investigation, the predominant Co–Fe oxide loaded on the SBA-15 support was the mixed oxide composite CoFe_2O_4 , which provided the active catalytic sites of CoFe/SBA-15. This catalyst has a moderate RhB adsorption capacity in aqueous solutions, and high catalytic activity and stability, reflected by the achieved RhB degradation of more than 98% and Co leaching of

Table 2

Rate constants for first-order kinetics of organic compound degradation in the presence of Co-loaded catalysts and PMS.

Catalyst	Model compound	Rate constant k_1 (min^{-1})	R^2	Ref.
Co/activated carbon	Phenol	0.125	0.991	[19]
Co/carbon-aerogel	Phenol	0.0289	0.992	[20]
Co/carbon-xerogel	Phenol	0.0916	0.982	[21]
CoFe_2O_4 /grapheme oxide	Phenol	0.1001	0.982	[22]
Co/red mud	Phenol	0.0371	—	[27]
Co/fly ash	Phenol	0.00513	—	[27]
Co/mesoporous MnO_2	Phenol	0.0425	0.996	[29]
Co/resin	Monuron (herbicide)	0.110	0.950	[26]
Co/SBA-15	RhB	0.063	0.971	[30]
CoFe/SBA-15	RhB	0.042	0.995	This work

Table 3
Quenching tests with different molar ratio of quenching agent/PMS.

Molar ratio of quenching agent/PMS	RhB removal (%)	
	EtOH	TBA
0:1	97.1	97.1
4000:1	83.1	97.0
6000:1	73.8	97.2
8000:1	63.1	96.7

less than 32.4 $\mu\text{g/L}$. These results suggest that the mechanism of RhB removal from aqueous solutions in the presence of CoFe/SBA-15 and PMS is as follows.

where the subscripts bulk, BL, and interface indicate species in bulk solution, at the boundary layer, and on the solid–liquid interface, respectively; MS-Fe³⁺ and MS-Co²⁺ are the Fe³⁺ and Co²⁺ species, respectively, anchored to the SBA-15 support; MS-FeOH²⁺, MS-CoOH⁺, MS-CoO⁺, and RhB-SO₄^{•−} represent the reaction intermediates; and SO₄^{•−} interface is the generated active radical, which plays a crucial role in RhB degradation. Catalytic oxidation and adsorption both contribute to RhB degradation in the CoFe/SBA-15/PMS system.

3.5.2. Quenching tests

Quenching tests involving addition of *t*-butyl alcohol (TBA) and ethanol were performed to identify the dominant radical species formed during PMS activation by the catalyst (Table 3). The results show that TBA addition did not greatly hinder RhB degradation, even at high concentrations. This implies that there were almost no hydroxyl radicals (OH[•]). However, with

ethanol addition, the degradation efficiency gradually decreased to 63.1%, which is far less than the original value. These results suggest that in the CoFe/SBA-15 and PMS system the active radical species are sulfate radicals (SO₄^{•−}) [7].

3.6. Reusability of CoFe/SBA-15 catalyst

3.6.1. Effects of different regeneration techniques

The reusability of the CoFe/SBA-15 catalyst was evaluated, using 10Co9.5Fe/SBA-15-700 as an example, with PMS as the oxidant. The regenerated 10Co9.5Fe/SBA-15-700 catalyst was immediately added to the RhB solution to initiate the reaction for each recycling run. Two different regeneration techniques were used. In the first one, the virgin catalyst was wrapped in a polytetrafluoroethylene membrane, which we used in a previous investigation as the wrapper for a powdery catalyst. After the first run, the used catalyst was thoroughly washed with ethanol and distilled water, respectively, and dried at 80 °C for 2 h to remove ethanol and water before the next run [30]. The recycling performance of the catalyst regenerated using this method is shown in Fig. 14(a). It shows that RhB degradation and Co leaching decreased from 95% to 63% and from 30 $\mu\text{g/L}$ to an undetected level, respectively, in the fourth run. The reduction in RhB degradation can be ascribed to deposition of more carbonaceous intermediates of RhB degradation on the active sites of the catalyst with increasing run number, and the Co leaching decreases because of leaching of loosely bound active species during the initial recycling runs.

The second regeneration technique is as follows. The used catalyst was recovered by magnetic separation, washed with distilled water, dried at room temperature, and calcined at a fixed temperature for a given period of time. Figure 14(b) shows the effects of the regeneration conditions on the catalyst reusability. The figure shows that the catalysts regenerated by calcination maintained high catalytic activities, with RhB removals exceeding 95%; this suggests that the carbonaceous intermediates of RhB degradation attached to the active sites of the catalyst can be removed by calcination for 1–3 h at 400–700 °C. Co leaching decreased significantly from 220 to 80

Fig. 14. Effects of different regeneration techniques on recycling performance of 10Co9.5Fe/SBA-15-700 catalyst. (a) Membrane; (b) Magnetic. Reaction condition: C_{RhB} 5.0 mg/L, 10Co9.5Fe/SBA-15-700 0.10 g/L, PMS/RhB molar ratio 20:1, 25 °C, 2 h, no solution pH adjustment.

Fig. 15. Recycling performance of 10Co9.5Fe/SBA-15-700 catalyst. Reaction condition: C_{RhB} 5.0 mg/L, 10Co9.5Fe/SBA-15-700 0.10 g/L, PMS/RhB molar ratio 20:1, 25 °C, 2 h, no solution pH adjustment.

μg/L below as the calcination temperature increased from 400 to 500 °C above, while keeping the calcination time at 3 h, and decreased from 100 μg/L to less than 80 μg/L when the calcination time was increased from 1 to 3 h, at 700 °C. A comparison of the various combinations of calcination temperature and time shows that the best combination was calcination at 500 °C for 3 h. The maximum RhB degradation, i.e., 95%, and lowest Co leaching, i.e., 53.5 μg/L, were achieved using the catalyst regenerated under these conditions.

3.6.2. Consecutive reuse of FeCo/SBA-15 catalyst

The reusability results for 10Co9.5Fe/SBA-15-700 are shown in Fig. 15. The used catalyst was regenerated by calcination at 500 °C for 3 h, based on the test results above. Figure 15(a) shows that the RhB degradation was more than 84% for 10 consecutive runs; this is attributed to activation of the catalytic sites by effective removal of carbonaceous deposits on the catalyst surface by calcination. The Co leaching remained below 72.1 μg/L (Fig. 15(a)), and Fe leaching was less than 35 μg/L (Fig. 15(b)). These results show the high stability of the 10Co9.5Fe/SBA-15-700 catalyst and the effectiveness of regeneration by calcination. As discussed above, the predominant Co–Fe oxide loaded on SBA-15 was the composite CoFe_2O_4 , in which the molar ratio of Co/Fe is 1:2. However, 10Co9.5Fe/SBA-15 has a 1:1 Co/Fe molar ratio, and the excess Co in 10Co9.5Fe/SBA-15 leads to a higher leaching concentration for Co than for Fe; this is also verified by Fig. 15.

4. Conclusions

A heterogeneous catalyst CoFe/SBA-15 was synthesized and characterized. The effects of the CoFe/SBA-15 preparation conditions on the catalytic performance, the kinetics and mechanism of catalytic oxidative degradation of RhB in the presence of CoFe/SBA-15 and PMS, and the reusability of the catalyst were investigated. The major Co–Fe species loaded on the support was the composite CoFe_2O_4 , which was present inside and outside the SBA-15 pores, and provided the active sites of the catalyst. 10Co9.5Fe/SBA-15-700 had a smaller sur-

face area, pore volume, and pore diameter than SBA-15, and a magnetic intensity of 8.3 emu/g, making it suitable for magnetic separation. It existed in the form of rod-like aggregates of diameter greater than 0.25 μm. It showed the maximum catalytic activity and stability, giving RhB degradation of more than 96% and Co leaching of less than 32.4 μg/L. The catalytic oxidative degradation of RhB in the FeCo/SBA-15-PMS system obeyed first-order kinetics, and the degradation rate increased with increasing CoFe/SBA-15 and PMS dosages, and with decreasing initial reactant concentrations. CoFe/SBA-15 maintained high catalytic activity and good stability during 10 recycling runs, with RhB degradation greater than 84%, Co leaching less than 72.1 μg/L, and Fe leaching less than 35 μg/L being achieved for each run. CoFe/SBA-15 combined with PMS has promising potential applications in removing non-biodegradable organics such as RhB in water.

References

- [1] Malato S, Blanco J, Richter C, Braun B, Maldonado M I. *Appl Catal B*, 1998, 17: 347
- [2] Chamarro E, Marco A, Esplugas S. *Water Res*, 2001, 35: 1047
- [3] Anipsitakis G P, Dionysiou D D. *Environ Sci Technol*, 2003, 37: 4790
- [4] Cheng M M, Ma W H, Li J, Huang Y P, Zhao J C, Wen Y X, Xu Y M. *Environ Sci Technol*, 2004, 38: 1569
- [5] Chen X Y, Chen J W, Qiao X L, Wang D G, Cai X Y. *Appl Catal B*, 2008, 80: 116
- [6] Neta P, Huie R E, Ross A B. *J Phys Chem Ref Data*, 1988, 17: 1027
- [7] Anipsitakis G P, Dionysiou D D. *Environ Sci Technol*, 2004, 38: 3705
- [8] Anipsitakis G P, Stathatos E, Dionysiou D D. *J Phys Chem B*, 2005, 109: 13052
- [9] Chan K H, Chu W. *Water Res*, 2009, 43: 2513
- [10] Yang Q J, Choi H, Al-Abed S R, Dionysiou D D. *Appl Catal B*, 2009, 88: 462
- [11] Ding Y B, Zhu L H, Huang A Z, Zhao X R, Zhang X Y, Tang H Q. *Catal Sci Technol*, 2012, 2: 1977
- [12] Su S N, Guo W L, Leng Y Q, Yi C L, Ma Z N. *J Hazard Mater*, 2013, 244–245: 736
- [13] Yang Q J, Choi H, Dionysiou D D. *Appl Catal B*, 2007, 74: 170
- [14] Yang Q J, Choi H, Chen Y J, Dionysiou D D. *Appl Catal B*, 2008, 77:

Graphical Abstract

Chin. J. Catal., 2015, 36: 1785–1797 doi: 10.1016/S1872-2067(15)60939-1

CoFe/SBA-15 catalyst coupled with peroxydisulfate for the heterogeneous catalytic degradation of dye rhodamine B in water

Longxing Hu*, Fan Yang, Lianpei Zou, Hang Yuan, Xing Hu
Shanghai University

Rhodamine B (RhB) in solution was adsorbed by CoFe/SBA-15 that activated PMS; Co^{2+} contributed to electron transfer and the sulfate radicals produced attacked the RhB molecules.

- 300
- [15] Zhang W, Tay H L, Lim S S, Wang Y S, Zhong Z Y, Xu R. *Appl Catal B*, 2010, 95: 93
- [16] Shukla P, Sun H Q, Wang S B, Ang H M, Tade M O. *Sep Purif Technol*, 2011, 77: 230
- [17] Liang H W, Ting Y Y, Sun H Q, Ang H M, Tade M O. *J Colloid Interf Sci*, 2012, 372: 58
- [18] Zhu Y Q, Chen S, Quan X, Zhang Y B. *RSC Adv*, 2013, 3: 520
- [19] Shukla P R, Wang S B, Sun H Q, Ang H M, Tade M. *Appl Catal B*, 2010, 100: 529
- [20] Hardjono Y, Sun H Q, Tian H Y, Buckley C E, Wang S B. *Chem Eng J*, 2011, 174: 376
- [21] Sun H Q, Tian H Y, Hardjono Y, Buckley C E, Wang S B. *Catal Today*, 2012, 186: 63
- [22] Yao Y J, Yang Z H, Zhang D W, Peng W C, Sun H Q, Wang S B. *Ind Eng Chem Res*, 2012, 51: 6044
- [23] Shi P H, Su R J, Wan F Z, Zhu M C, Li D X, Xu S H. *Appl Catal B*, 2012, 123-124: 265
- [24] Shi P H, Su R J, Zhu S B, Zhu M C, Li D X, Xu S H. *J Hazard Mater*, 2012, 229-230: 331
- [25] Shukla P, Wang S B, Singh K, Ang H M, Tade M O. *Appl Catal B*, 2010, 99: 163
- [26] Chu W, Choy W K, Kwan C Y. *J Agr Food Chem*, 2007, 55: 5708
- [27] Saputra E, Muhammad S, Sun H Q, Ang H M, Tade M O, Wang S B. *Catal Today*, 2012, 190: 68
- [28] Hu L X, Yang X P, Dang S T. *Appl Catal B*, 2011, 102: 19
- [29] Shukla P, Sun H Q, Wang S B, Ang H M, Tade M O. *Catal Today*, 2011, 175: 380
- [30] Hu L X, Yang F, Lu W C, Hao Y, Yuan H. *Appl Catal B*, 2013, 134-135: 7
- [31] Liang H W, Sun H Q, Patel A, Shukla P, Zhu Z H, Wang S B. *Appl Catal B*, 2012, 127: 330
- [32] Qi F, Chu W, Xu B B. *Appl Catal B*, 2013, 134-135: 324
- [33] Zhao D Y, Huo Q S, Feng J L, Chmelka B F, Stucky G D. *J Am Chem Soc*, 1998, 120: 6024
- [34] Jun S, Joo S H, Ryoo R, Kruk M, Jaroniec M, Liu Z, Ohsuna T, Terasaki O. *J Am Chem Soc*, 2000, 122: 10712
- [35] Wang Y R, Chu W. *Ind Eng Chem Res*, 2011, 50: 8734
- [36] Martı nez-de la Cruz A, Garcı a P rez U M. *Mater Res Bull*, 2010, 45: 135
- [37] Hou M F, Liao L, Zhang W D, Tang X Y, Wan H F, Yin G C. *Chemosphere*, 2011, 83: 1279
- [38] Merouani S, Hamdaoui O, Saoudi F, Chiha M. *Chem Eng J*, 2010, 158: 550
- [39] Bai C P, Xiong X F, Gong W Q, Feng D X, Xian M, Ge Z X, Xu N. *Desalination*, 2011, 278: 84
- [40] Du L, Wu J, Hu C W. *Electrochim Acta*, 2012, 68: 69
- [41] Marler B, Oberhagemann U, Vortmann S, Gies H. *Microporous Mater*, 1996, 6: 375
- [42] Kim S J, Lee S W, An S Y, Kim C S. *J Magn Magn Mater*, 2000, 215-216: 210
- [43] Melero J A, Calleja G, Martı nez F, Molina R, Pariente M I. *Chem Eng J*, 2007, 131: 245
- [44] Liang H W, Sun H Q, Patel A, Shukla P, Zhu Z H, Wang S B. *Appl Catal B*, 2012, 127: 330
- [45] Ramirez J H, Maldonado-Hodar F J, P rez-Cadenas A F, Moreno-Castilla C, Costa C A, Madeira L M. *Appl Catal B*, 2007, 75: 312
- [46] Anipsitakis G P, Dionysiou D D, Gonzalez M A. *Environ Sci Technol*, 2006, 40: 1000
- [47] Wu T X, Liu G M, Zhao J C, Hidaka H, Serpone N. *J Phys Chem B*, 1998, 102: 5845
- [48] He Z, Yang S G, Ju Y M, Sun C. *J Environ Sci*, 2009, 21: 268

Co-Fe/SBA-15与过一硫酸盐联用非均相催化降解水中染料罗丹明B

胡龙兴*, 杨帆, 邹联沛, 袁航, 胡星

上海大学环境与化学工程学院, 上海200444

摘要: 由于硫酸根自由基($\text{SO}_4^{\bullet-}$)的强氧化性, 基于 $\text{SO}_4^{\bullet-}$ 的高级氧化技术受到人们的高度关注. 采用过渡金属活化过一硫酸盐(PMS)产生 $\text{SO}_4^{\bullet-}$ 用以分解有机物, 反应体系简单, 反应条件温和, 且不需要额外的能量供给, 因此, 成为人们优先选用的方法, 其中, 采用高效、环境友好的非均相过渡金属催化剂活化PMS处理难降解有机物成为研究热点. 本文研究了非均相CoFe/SBA-15-PMS体系对水中难降解染料罗丹明B(RhB)的降解. 以SBA-15为载体, $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ 和 $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ 为前驱物, 采用一步等体积浸渍法制备了CoFe/SBA-15, 通过X射线衍射(XRD)、 N_2 吸附-脱附、扫描电镜(SEM)、能谱(EDS)、透射电镜(TEM)和振动样品磁强计(VSM)等对其进行了表征. 考察了焙烧温度、Co与Fe的负载量对CoFe/SBA-15催化性能的影响和该催化剂的重复使用性能, 还考察

了RhB降解动力学及催化剂CoFe/SBA-15投加量、氧化剂PMS投加量和反应物(RhB和PMS)初始浓度对其性能的影响,探讨了RhB的降解机理. 结果表明: 对于催化剂CoFe/SBA-15, 合成焙烧后在SBA-15上负载的Fe、Co化合物主要是 CoFe_2O_4 复合物, 它作为催化剂的活性中心负载在SBA-15的孔道内外. 制备的焙烧温度对CoFe/SBA-15催化性能几乎无影响, 但对Co浸出影响显著. 与SBA-15相比, 催化剂10Co9.5Fe/SBA-15-700 (Co和Fe负载量分别为10 wt%和9.5 wt%, 焙烧温度700 °C)的比表面积、孔体积和孔径均减小, 分别为 $506.1 \text{ m}^2/\text{g}$, $0.669 \text{ cm}^3/\text{g}$ 和 7.4 nm , 但仍然保持SBA-15的有序六方介孔结构. 该催化剂以棒状体的聚集态存在, 聚集体直径大于 $0.25 \mu\text{m}$, 其磁化强度为 8.3 emu/g , 因此, 可通过外磁铁容易地从水中分离. 相比之下, 10Co9.5Fe/SBA-15-700具有最佳的催化性能和稳定性, 可使RhB的降解率达到96%以上, Co的浸出量小于 $32.4 \mu\text{g/L}$. 在CoFe/SBA-15和PMS共存下, RhB的降解符合一级动力学方程, RhB降解速率随CoFe/SBA-15和PMS投加量的增加和初始反应物浓度的减小而提高. 淬灭实验结果表明, 在CoFe/SBA-15, PMS和RhB水溶液体系中, 存在的主要活性自由基为 $\text{SO}_4^{\cdot-}$, 它是由CoFe/SBA-15活化PMS产生的, 对RhB的降解起决定性的作用. RhB降解过程的UV-vis结果表明, RhB的降解途径主要是蒽环打开, $\text{SO}_4^{\cdot-}$ 优先攻击RhB的有色芳香烃环, 然后RhB进一步分解为小分子有机物. CoFe/SBA-15循环使用10次仍能保持高催化活性和稳定性, 在每次反应中RhB的降解率均大于84%, Co和Fe的浸出量均分别小于 72.1 和 $35 \mu\text{g/L}$. CoFe/SBA-15作为高效、环境友好的非均相催化剂可有效地活化PMS产生 $\text{SO}_4^{\cdot-}$ 降解水中RhB, 具有实际应用的潜力.

关键词: 钴; 铁; SBA-15; 过一硫酸盐; 罗丹明B降解, 高级氧化技术, 硫酸根自由基

收稿日期: 2015-05-18. 接受日期: 2015-06-17. 出版日期: 2015-10-20.

*通讯联系人. 电话/传真: (021)66137771; 电子信箱: hulxhbb@shu.edu.cn

基金来源: 大学创新研究团队项目(IRT 13078).

本文的英文电子版由Elsevier出版社在ScienceDirect上出版(<http://www.sciencedirect.com/science/journal/18722067>).