



Activity assessment of direct synthesized Fe-SBA-15 for catalytic ozonation of oxalic acid



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ABSTRACT

Highly ordered Iron-doped SBA-15 mesoporous material (Fe-SBA-15), which was synthesized via a direct hydrothermal method under weak acid condition, was used as heterogeneous catalyst for the ozonation of oxalic acid in aqueous solution. The results indicated that Fe doping significantly improved the catalytic activity of SBA-15, a high oxalic acid removal of 86.6% was achieved under the chosen condition, only 30.2% for SBA-15/O₃ process. The major operating variables including Si/Fe ratio in catalyst, initial pH value and radical scavenger were also studied for catalytic reaction mechanism. The active sites of Fe-SBA-15 increased with iron doping content and Fe-SBA-15 significantly influenced ozone concentration in aqueous solution. The catalytic efficiency was mainly affected by radical scavenger and the pH value of solution, which illustrated that the catalytic ozonation process followed free radical mechanism, and the surface reaction played a critical role for oxalic acid degradation. The stability of Fe-SBA-15 was verified by the reused experiments. The XRD and BET tests also demonstrated that Fe-SBA-15 retained highly ordered 2D-hexagonal mesoporous structure and large surface area after reused. Fe-SBA-15 was a promising catalyst for catalytic ozonation of oxalic acid.

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1. Introduction

Heterogeneous catalytic ozonation, a strong oxidation process based on ozonation, has attracted much attention in wastewater treatment field due to its potentially higher effectiveness in the elimination of organic compounds at ambient temperature and pressure [1–6]. Generally accepted mechanism for heterogeneous catalytic ozonation was based on an ozone decomposition reaction followed by the generation of hydroxyl radical. And chemisorption on the surface of catalyst, either chemisorption of ozone, organic compound or sorption of both substances, was thought to be essential for the catalytic reaction [7]. To enhance the generation of hydroxyl radical, catalysts, such as metal oxides, metals or metal oxides on metal oxide supports, were employed in catalytic process.

To date, mesoporous siliceous materials (SBA-15 and MCM-41) have attracted great attention in various fields especially for catalysis and adsorption for their high surface areas [4,8–11]. Compared with MCM-41, SBA-15 was characterized for its larger and tailored pore sizes, thicker walls and much higher hydrother-

mal and thermal stability [12–16]. However, SBA-15 is inert in catalytic reaction due to the absence of heteroatom active sites, hence it needs to be introduced with active sites to improve the catalytic activity. Most of the reported literatures were focused on post-synthetic grafting modification of SBA-15 [5,17–20] and Fe loading SBA-15 has been synthesized by a hydrothermal method in our previous work [21]. But the post-treatment may show low dispersion of metal oxides or result in partial blocking of mesoporous, which may reduce the specific surface area or even have a negative effect on the catalysts [22,23]. Therefore, some studies have been attempted to introduce metal ions into the framework of SBA-15, to prepare catalysts with highly isolated catalytic active sites. Although there have been a few papers reporting the direct synthesis of metals-incorporated SBA-15, such as Ln-SBA-15, V-SBA-15, Ce-SBA-15 [13,24,25]. It is still a challenge for incorporating metal ions into the framework of SBA-15 at a strong acidic condition where the metal-O-Si bond is hardly formed [13].

Herein, we reported the direct synthesis of iron doping SBA-15 (Fe-SBA-15) by a hydrothermal synthesis method in weak acidic medium, and its catalytic activity was assessed by ozonation of oxalic acid, a typical refractory intermediate product to conventional chemical oxidation including ozonation. This study focused on the influence of initial pH value and the relationship between

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oxalic acid adsorption and its removal by Fe-MCM-41. Also, the degradation mechanism was deduced.

2. Experimental

2.1. Materials and reagents

Tetraethyl orthosilicate (TEOS), ferric nitrate ($\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$) and methanol were purchased from Sinopharm Chemical Reagent Co. Ltd. (Shanghai, China). The triblock copolymer $\text{EO}_{20}\text{PO}_{70}\text{EO}_{20}$ (Pluronic P123, MW = 5800) was provided by Sigma–Aldrich. Oxalic acid, tert-butanol (TBA), hydrochloric acid (HCl), sulfuric acid (H_2SO_4) and sodium hydroxide (NaOH) were obtained from Tianjin Damao Chemical Agent Factory (Tianjin, China). All chemicals were analytical. All solutions were prepared with deionized water.

2.2. Preparation of Fe-SBA-15

Fe-SBA-15 was synthesized via a hydrothermal method under weak acid medium. P123, TEOS and $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ were used as template, silicon source and Fe source, respectively. 4 g P123 was dispersed in 30 ml water and 2 ml 2 M HCl solution at 313 K for 3 h, followed by the addition of 60 ml water and the mixture was stirred for 2 h. Thereafter, appropriate amount of $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ was added directly to the solution with stirring for 1 h. After pH value was adjusted to 2.5, 9.0 g TEOS was added dropwise. Then the mixture was continuously stirred for 24 h at 313 K, transferred into a Teflon-lined autoclave and aged for 24 h at 373 K. The product was then filtered, washed, and dried at 353 K. Then the sample was calcined at 823 K in air for 6 h to get Fe-SBA-15. For comparison, SBA-15 was also prepared at the same method without adding $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$.

2.3. Catalytic ozonation procedure

The catalytic ozonation procedure was carried out in a 1.3 L cylindrical reactor ($h = 500$ mm, $\Phi = 60$ mm) made of borosilicate glass. The reaction was maintained at desirable temperatures by circulation water from a thermostatic bath (SDC-6, Ningbo, China). Ozone was produced in situ from pure oxygen (1.2 L min^{-1}) by a DHX-SS-1G ozone generator (made in China). 1.2 L 20 mg L^{-1} oxalic acid solution and 0.24 g catalyst were added into the reactor, and ozone (100 mg h^{-1} output) was continuously fed to the solution through a porous glass plate at the bottom of the reactor. All experiments were conducted at initial solution pH (pH = 3.7) except that in 3.4.3.

2.4. Analytical procedures

XRD measurements of the samples were carried out using $\text{Cu K}\alpha$ radiation in the 2θ ranges of 0.6 – 3.0° (low angle) on a BRUKER D8 ADVANCE X-ray diffractometer. The N_2 adsorption–desorption isotherms were carried out at 77 K on a Quantasorb surface area analyzer (Micromeritics, ASAP2020, USA).

Water samples were first filtered by a 0.45 μm prefilter. Oxalic acid concentration was quantified with a high performance liquid chromatography (HPLC, LC10A, Shimadzu, Japan) using a Diamonsil 5U C18 column (250 mm \times 4.6 mm, Dikma technologies). The wavelength of UV/visible detector (SPD – 10AV) was set at 210 nm. The mobile phase was composed of methanol and water at 90:10 (v:v) with flow rate controlled at 1.0 ml min^{-1} . Ozone concentration in aqueous solution was measured by using the indigo method. pH_{PZC} (pH at point of zero charge) of samples was measured by using the potentiometric titration method.

3. Results and discussion

3.1. Synthesis and characterization

Fe-SBA-15 was successfully synthesized via a direct hydrothermal method by adjusting pH value of the solution to 2.5 accurately, which was critical for the introduction of Fe into the framework of SBA-15. To observe the crystalline phase and structure features of samples, the prepared substances were analysed by XRD and BET. As shown in Fig. 1, both samples showed characteristic diffraction peaks at (100), (110) and (200), indicating 2D-hexagonal mesoporous structure of Fe-SBA-15 [12]. The N_2 adsorption–desorption isotherm and the pore size distribution curve of samples (Fig. 2) showed type IV isotherms with H1 hysteresis loop, which were typical for the highly ordered mesoporous material with uniform mesopore size distribution, and it had a high surface area of 663.2 m^2 g^{-1} . It was noted that mesoporous silica materials synthesized under weak acidic conditions do not show well-ordered structures [22]. So the ordering structure may be partly due to the salt effect of iron precursor, the hydrolysis of ferric nitrate produces protons making the increasing acidity of the reactant [26,27]. Table 1 also summarized the textural properties of two materials. Since the radius of Fe^{3+} is larger than that of Si^{4+} , the slight decrease of surface area and pore volume after Fe doping indicated that Fe was incorporated into the framework of SBA-15 [26].

3.2. Catalytic activity assessment of Fe-SBA-15

According to the literature, oxalic acid is one of the most common final oxidation products from organic compounds degradation, with a high refractory character relative to single ozonation [28–30]. So it was chosen as a model compound to study the catalytic activity of Fe-SBA-15. As shown in Fig. 3, Fe-SBA-15 (mole ratio Si/Fe = 80) showed high catalytic activity for ozonation of oxalic acid when compared to O_3 or SBA-15/ O_3 . Specifically, oxalic acid was a small chain carboxylic acid with high refractory towards ozone, only 10.9% removal was achieved at 60 min reaction time. In addition, oxalic acid was also poorly oxidized under the operating condition employed in the presence of SBA-15, only 30.2% removal was achieved. The result demonstrated that SBA-15 had low catalytic activity, and it needs to be introduced with active sites to improve its catalytic activity. When Fe-SBA-15 was added into the ozonation system, the removal of oxalic acid significantly increased. A high removal of 64.6% was carried out with the reaction time continue to 60 min, 5.9 times higher than O_3 , 2.1 times

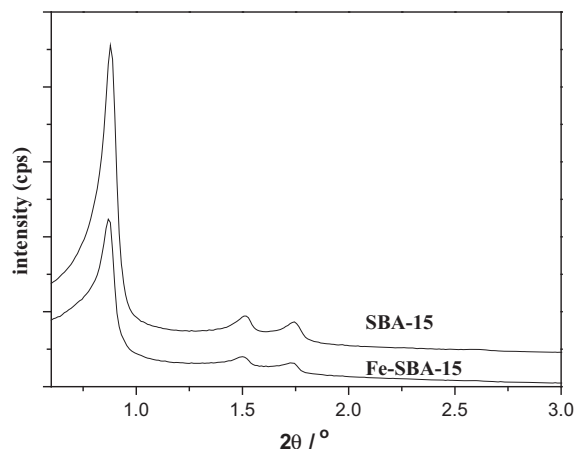


Fig. 1. The low angle XRD patterns of SBA-15 and Fe-SBA-15.

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