



A novel solid acid coating catalyst on Q235 carbon steel for Fenton-like oxidation of phenol under circumneutral pH



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ABSTRACT

Novel amorphous Fe₃O₄/FePO₄/ZrO₂ ceramic coatings as solid acid with porous structure were successfully synthesized in the phosphate electrolyte containing K₂ZrF₆ via plasma electrolytic oxidation (PEO) technique and characterized by scanning electron microscopy, X-ray diffraction and X-ray photoelectron spectroscopy. The surface acidic property was investigated by NH₃-TPD method. The results showed that the pore size and the intensity of pore interconnection of amorphous Fe₃O₄/FePO₄/ZrO₂ ceramic coating with solid acid property, increased with the increase of the K₂ZrF₆ dosage from 0.5 g to 2.0 g in the phosphate electrolyte. The Fenton-like performance of PEO coating catalysts was investigated by degradation of phenol under circumneutral pH. It was found that phenol removal efficiency decreased with the adding of K₂ZrF₆ amount from 0.5 g to 2.0 g except no catalytic activity of coating prepared without K₂ZrF₆, and Fenton-like PEO coating catalyst prepared with 0.5 g K₂ZrF₆ exhibited a superior catalytic activity which could degrade phenol thoroughly within 2 min under circumneutral pH. The strong acid sites played a dominant role in enhancing the Fenton-like catalytic activity. The excellent catalytic activity of PEO coating prepared in the phosphate electrolyte containing K₂ZrF₆ endowed it potential application in wastewater treatment.

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1. Introduction

Over the last decades, large amount of the toxic wastewater containing phenolic compound from industrial section such as petroleum refining and dyes, are discharged into the environment which are biorefractory and have great damage to ecosystem and human beings. Hence, it is essential for us to pursue efficient, inexpensive and green technology for biorecalcitrant organic pollutants treatment in the wastewater. Recently, the research finds that Fenton-like reaction is verified to be an ideal technology for biorecalcitrant and harmful organic pollutants removal, which is based on the produced ·OH with redox potential of 2.8 V (vs. NHE) to oxidize and mineralize organic molecules. So far, Fenton-like process mainly adopted Fe-bearing materials such as iron oxides,

zero-valent iron, and iron supported on zeolite, clay and carbon materials et al., as heterogeneous catalyst to catalyze H₂O₂ for ·OH generation [1–7].

However, two aspects limit their wide application: Firstly, most of Fenton-like catalyst has no or poor catalytic activity under circumneutral pH [7–9]. Secondly, almost all of the reported Fenton-like catalysts exist in the form of powder; While the major obstacle of the powder is the requirement of filtration or centrifugation for recovering the catalyst from the reaction solution which increases the treatment cost; Moreover, it is difficult to remove the smallest catalyst particles from the solution which leads to the loss of catalyst [10].

In order to widen the working pH range of Fenton-like catalysts so that they can keep higher catalytic activity under circumneutral pH, some researchers tried to prepare solid acid catalyst which could introduce acid sites and create acidic microenvironment on the surface, and then enhance catalytic activity. For example, Wu yujiao and his group [11] synthesized porous solid superacid SO₄²⁻/Fe_x²⁺-Zr_xO₃ Fenton-like catalyst which presented high efficient catalytic activity under pH 6.0 and still had catalytic activity even under alkaline condition; Du et al. [12] prepared a mesoporous

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sulfur-modified iron oxide (MS-Fe) and studied its Fenton-like oxidation of bisphenol A; The results revealed that the high catalytic activity could be obtained at different initial pH (pH 3.0–9.0). In addition, to solve the difficulty of catalyst recycling, immobilized iron oxide coating was reported. For example, Jang et al. [13] prepared iron oxide nanotube film on iron foil through anodization and investigated its Fenton-like catalytic activity.

Inspired by the above ideas, the thought to prepare the coating catalyst with solid acid property was proposed for solving drawbacks of the narrow working pH and recycling difficulty of catalyst. Yet although many methods for preparing immobilized coating catalyst were developed, such as atomic layer deposition [14], chemical vapor deposition [15], hydrothermal method [16] and so on, high cost, time-consuming and process complexity restrict them large scale application.

Plasma electrolytic oxidation (PEO) method with the advantages of economic efficiency, environmental friendliness has been widely used to fabricate various functional coating such as thermal control, corrosion and wear resistance, biomedicine, decorative coating and photocatalysis, on Al, Mg, Ti alloys and carbon steel [17–30]. However, ceramic coating on Q235 carbon steel prepared in phosphate electrolyte containing K_2ZrF_6 by plasma electrolytic oxidation was never mentioned in the published literature so far.

In this paper, Fe_3O_4 -based ceramic coating with solid acid property was first successfully prepared in phosphate electrolyte containing K_2ZrF_6 by PEO technique and was used as Fenton-like catalyst to degrade phenol target pollutant. The phenol degradation experiment showed that PEO coating catalyst with high catalytic activity for H_2O_2 activation was obtained. The influence of PEO coatings prepared with different K_2ZrF_6 content on phenol degradation was investigated.

2. Experimental

2.1. Chemicals and materials

Sodium hexametaphosphate ($Na_6P_6O_{18}$), Sodium tripolyphosphate ($Na_5P_3O_{10}$), K_2ZrF_6 , Na_2SO_4 , phenol and hydrogen peroxide (H_2O_2 , 30 wt %) were purchased from Sinopharm Chemical Reagent Co., Ltd. All chemicals were obtained without further purification. All solutions used were prepared with deionized water.

2.2. Preparation of Fenton-like ceramic coating

Rectangular Q235 carbon steel (20 mm × 20 mm × 0.5 mm) was used as anode for PEO. Before PEO, the sample was polished with sandpaper and then washed with deionized water, absolute ethanol, finally dried with a dryer. A home-made unipolar pulsed DC power source with pulse peak current waveform was utilized for PEO process and stainless steel electrolyser with recirculating cooling water system was served as cathode. The electrolyte was comprised of 13.35 g/L $Na_6P_6O_{18}$, 2.65 g/L $Na_5P_3O_{10}$, 10 g/L Na_2SO_4 and different content of K_2ZrF_6 (0.0 g, 0.5 g, 1.0 g, 1.5 g and 2.0 g). During PEO, pulse peak current and frequency was 96 A, 2000 Hz respectively and reaction time was 9 min except the coating prepared with 0.0 g K_2ZrF_6 , the reaction time of which was 30 min. The electrolyte temperature was maintained 25 °C by cooling-water system. After PEO, the as-prepared PEO coatings were taken off and washed with deionized water and then dried with a dryer.

2.3. Catalyst characterization

The surface morphology of as-prepared coatings was studied with SEM (Quanta 200FEG) working at 20 kV. X-ray diffraction (XRD) data were collected using a Rigaku D/max-RB diffractometer

using Cu K_{α} radiation ($\lambda = 0.154$ nm). The surface chemical compositions were determined with X-ray photoelectron spectroscopy (XPS) (PHI 5700 ESCA System) with a monochromatic Al K α source (1486.6 eV). In order to evaluate the acidic property of the catalyst, temperature-programmed desorption of ammonia (NH_3 -TPD) was carried out on Finetec FINESORB-3010 instrument. The powder sample which was from ceramic coating, was used for NH_3 -TPD measurement. Fourier transform infrared (FT-IR) spectra were measured by employing a Nicolet 750 FT-IR spectrometer.

2.4. Phenol degradation procedure

Phenol degradation experiment was performed with 50 mL 35 mg/L phenol solution in a 100 mL beaker under a constant temperature water bath (303 K). The initial pH of the solution was 6.0 which was close to neutral pH and called as circumneutral pH. The as-prepared PEO coating with 6 cm² was immersed into the phenol solution and 0.034 mL hydrogen peroxide (H_2O_2 , 30 wt. %) was added, and then the degradation reaction was initiated under constant stirring speed. During degradation, a given amount of sample was removed with a pipette at a certain time for phenol and leached Fe concentration measurement.

2.5. Sample analysis

Phenol concentration in the solution was measured with 4-aminoantipyrine at 510 nm on a UV/Vis spectrophotometer (Lambda XLS, PerkinElmer) [7,31]. The concentration of the ferrous ion and total iron leaching from the catalysts were evaluated by 1, 10-phenanthroline method [32,33]. The relative phenol concentration (C/C_0) corresponded to the relative absorbance (A/A_0) at 510 nm. C_0 and A_0 were the initial phenol concentration and absorbance respectively; C and A were phenol concentration and absorbance at given time respectively.

3. Results and discussion

3.1. Characterization of catalysts

The surface morphology of the as-prepared coatings in phosphate electrolyte containing different content of K_2ZrF_6 was shown in Fig. 1. It was noteworthy that without adding the K_2ZrF_6 , no discharge sparks was observed on the treated sample surface even the reaction time was extended to 30 min, but some substances were deposited on the substrate after the reaction; the SEM analysis indicated that the bulk substance and some flower-like materials comprised of nanosheets were deposited on the substrate surface, and the surface was uneven and wasn't porous structure which meant that the obtained coating was not the PEO coating in the only phosphate electrolyte without adding the K_2ZrF_6 . However, in the phosphate electrolyte containing K_2ZrF_6 the reaction was drastic and significant discharge sparks were observed; in addition, the obtained coatings with porous structure were formed due to the quenching effect of electrolyte and spark discharge suggested that the PEO coatings were successfully prepared after adding K_2ZrF_6 in the phosphate electrolyte. From Table 1 it could be known that P content in the coatings increased greatly after adding K_2ZrF_6 which indicated that the existence of K_2ZrF_6 in the phosphate electrolyte could facilitate the accumulation of phosphate on the substrate surface and then form the accumulated layer which is beneficial to fabricate PEO ceramic coating [34]. Hence, K_2ZrF_6 played a dominant role in fabricating the PEO coating.

The surface morphology and the average pore size of the PEO coatings were shown in Fig. 1b–e and Fig. 2. The average pore size was obtained through ImageJ software. The intensity of pore

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