Chemosphere 161 (2016) 446–453

Contents lists available at ScienceDirect

Chemosphere

journal homepage: www.elsevier.com/locate/chemosphere

Selective conversion of organic pollutant *p*-chlorophenol to formic acid using zeolite Fenton catalyst

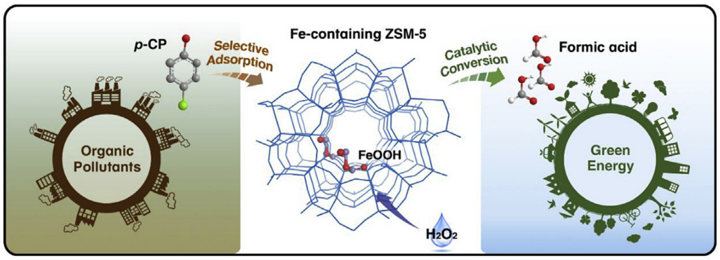
Chensi Shen [a, b], Jianqing Ma [b], Wanpeng Liu [b], Yuezhong Wen [b, *], Sadia Rashid [a]

[a] *College of Environmental Science and Engineering, Donghua University, Shanghai, 201620, China*
[b] *Institute of Environmental Science, Zhejiang University, Hangzhou, 310058, China*

HIGHLIGHTS

- A possible method for extracting formic acid from wastewater was investigated.
- A new aspect of Fe-containing ZSM-5 catalyst for pollutant resource was explored.
- Fast and controllable degradation of *p*-chlorophenol to formic acid was achieved.
- This catalyst can activate H_2O_2 to degrade phenol while avoiding over-oxidation.
- The extra-framework of coordination unsaturated Fe plays an important role.

GRAPHICAL ABSTRACT



ARTICLE INFO

Article history:
Received 29 December 2015
Received in revised form
7 July 2016
Accepted 12 July 2016
Available online 25 July 2016

Handling Editor: Jun Huang

Keywords:
Catalyst
Fenton-like reaction
Resource
Selective conversion

ABSTRACT

Effective remediation technologies which can converse the harmful organic pollutants to high-value chemicals are crucial both for wastewater treatment and energy regeneration. This study provides an evidence that extracting useful chemicals from wastewater is feasible through selective conversion of *p*-chlorophenol to high value formic acid as an example. The reported system works with a readily available Fe-containing ZSM-5 catalyst, water as the solvent and hydrogen peroxide as the oxidant. The yield of formic acid reached up to 50.7% when the Si/Al ratio of ZSM-5 was 80 and the Fe-content was 1.4%. By X-ray adsorption fine structure (XAFS), NH_3 temperature-programmed desorption (NH_3-TPD) technique, the pyridine adsorption Fourier-transition infrared (Py-IR) spectroscopy and adsorption measurements, it was concluded that the controllable degradation of *p*-CP could be approached through selective adsorption, the moderate Brønsted acid sites for H_2O_2 activation and the properly selective conversion control due to extra-framework coordination unsaturated sites (CUS) of Fe. This approach might provide a new avenue for the field of organic pollutant remediation.

1. Introduction

Nowadays, great effort is being done to make industrial wastewater fit for discharge and large amount of energy has been consumed in wastewater treatment in order to avoid further pollution of aquatic environments (McCarty et al., 2011; Xu et al.,

---

* Corresponding author.
E-mail address: wenyuezhong@zju.edu.cn (Y. Wen).

http://dx.doi.org/10.1016/j.chemosphere.2016.07.038
0045-6535/

2014; Shen et al., 2011; Liu et al., 2016). It should also be noted that the organic pollutant in wastewater is a kind of important energy source. The chemical energy of mixed wastewater has reached 16.8 kJ/L (Heidrich et al., 2011; Logan and Rabaey, 2012). Therefore, with increasing global energy demand and the environmental impacts of fossil fuels, the development of the "pollutant-to-resource" technology which can converse the harmful organic pollutants to energy resources has become an urgent issue (Ruhl et al., 2012; Yao et al., 2015). If the "pollutant-to-resource" technology is developed then not only the pollutants will be removed but renewable source of energy will also be provided.

An often-touted solution to this problem is the microbial electrochemical technologies (METs). For example, microbial fuel cells (MFCs) are promising approaches for capturing the energy in wastewater and have attracted much attention. Although microbial conversion is at present the main route for the "pollutant-to-resource" technology, energy recovery in METs to date still need to be improved, leading some to question whether they can ever compete with conventional processes (Heidrich et al., 2011). Another feasible route for wastewater is to produce useful chemicals with METs or other treatment technologies. Through comparing anaerobic digestion, MFCs, and microbial electrolysis cells (MECs), it has been proposed that production of chemicals can bring about a considerable environmental benefit to the overall treatment process (Logan and Rabaey, 2012). It is therefore necessary to explore alternative "pollutant-to-resource" technology to extract high-value chemicals from wastewater.

Advanced oxidation processes (AOPs) constitute a promising technology for wastewater treatment, especially for the degradation of non-easily removable organic compounds (Andreozzi et al., 1999; Wen and Jiang, 2001; Li et al., 2015b). During the AOP degradation, low-molecular-weight organic acids are recognized as the major products prior to mineralization (Boudenne and Cerclier, 1999; Zhu et al., 2012; Li et al., 2015a). Fittingly, formic acid has attracted considerable attention as suitable liquid source for hydrogen and as a potential hydrogen storage material due to its facile oxidation kinetics, high theoretical cell potential and low fuel crossover (Jiang and Wieckowski, 2012). If the organic pollutants can be selectively conversed to formic acid, considerable liquid fuels will be obtained as well as the hazardous materials will be decontaminated. But to the best of our knowledge, there was little AOP focus on the technology of "pollutant-to-resource", because AOPs is not the best process to achieve selective conversion of substrates in which the hydroxyl radicals generated are too reactive to control (Ikeda et al., 2007).

In general, heterogeneous catalytic oxidation is believed to occur when the species to be oxidized adsorb on the catalyst surface, and thus the actions at particle/solution interfaces are controlled by both relative redox energies and adsorption characteristics (Zhang et al., 2011). For the adsorption ability of catalyst towards the reacting components, it could be utilized for favoured enrichment of the target organic pollutants in the vicinity of the catalytic centers (Rashid et al., 2015), meanwhile the non-target consumers of the reactive species can be discriminated due to their weakly adsorption affinity. Therefore, facile degradation of organic pollutants, effective conversion of intermediates and weak adsorption of product are key requirements for efficient and selective catalysis conversion.

Exploiting this fact, we reported a new possibility for energy utilization, which can generate a large proportion of formic acid from selective conversion of the common organic pollutant. In order to explore the feasibility of a controllable degradation process which might achieve the goal of "pollutant-to-resource", *p*-chlorophenol which is a typical chemical compound or intermediate in chemical industry was selected as the model pollutant with the purpose of exploring. The Fe-containing ZSM-5 Fenton catalyst was used to activate H_2O_2 to degrade chlorophenol while suppressing complete mineralization in mild condition. And its applicability was evaluated in view of the yield, residual total organic carbon (TOC), as well as the reusability of the catalyst. Additionally, the possible mechanism proposed herein may be also used to account for the controllable conversion of *p*-CP.

2. Material and method

2.1. Materials

NH_4-ZSM-5 (Zeolyst International, Si/Al ratio = 23, 30, 50 and 80) was calcined at 450 °C for 4 h to obtain H-ZSM-5 (denoted as H-23, H-30, H-50 and H-80, respectively). The Fe-containing ZSM-5 zeolites were prepared by pore-volume impregnating $Fe(NO_3)_3 \cdot 9H_2O$ from its aqueous solution on H-ZSM-5, drying the impregnated mass in an air at room temperature for 24 h and then calcining in air at 450 °C for 4 h (denoted as Fe X-23, Fe X-30, Fe X-50 and Fe X-80, referring to different Fe-containing X% and Si/Al ratio). The chemistry reagent *p*-chlorophenol (*p*-CP), benzoquinone (BQ), hydroquinone (HQ), 4-chlorocatechol (CA), formic acid (ForAc), acetic acid (AceAc), maleic acid (MalAc), fumaric acid (FumAc), $Fe(NO_3)_3 \cdot 9H_2O$ and H_2O_2 (30% w/w) were obtained from Sigma-Aldrich and National Medicines Corporation Ltd. of China. Ultrapure water (18.23 MΩ) was used throughout this study. Other chemicals was of laboratory reagent grade and used without further purification.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns of the chitosan sample were measured using a Panalytical XPert Pro MPD diffractometer (Almelo, Netherland) with a Cu Kα ray source (λ = 1.54 A°). The scanning diffraction angle range was set at 10–80° and the scan rate was 2° (2θ) per minute with the spectra being recorded at 40 kV and 36 mA. Catalyst acidity was determined by the NH_3 temperature-programmed desorption (NH_3-TPD) technique, and the pyridine adsorption Fourier-transition infrared (Py-IR) spectroscopy, and the detailed processes were described in Text S3 in Supporting Information. The average pore diameter of the samples were determined with an ASAP-2020 Micromeritics equipment based on the adsorption isotherm. X-ray absorption fine structure (XAFS) and the synchrotron-based scanning transmission X-ray microscopy (STXM) was performed at beam-line BL14W1 and BL08U1 of the Shanghai Synchrotron Radiation Facility (SSRF) (Text S2 in Supporting Information).

2.3. General procedure for p-CP conversion

All the *p*-CP conversion experiments were performed in 50 mL flasks, which were sealed and agitated at 100 rpm in a thermostatic shaker maintained at 25 °C. The typical reaction mixture was initiated with 20 mL of *p*-CP at 20 mmol/L, 0.05 g of zeolite catalyst and 0.04 mL 30% (w/w) H_2O_2 at the neutral condition. In case of the adsorption experiments, the initial mixture was same as the typical reaction, but without H_2O_2. At certain time intervals, aliquots of 1.0 mL sample were periodically withdrawn and filtrated through 0.22 μm syringe filter immediately, and the catalase was used to stop the reaction (complete consumption of H_2O_2). In the durability tests, the used zeolite samples were filtered from aqueous solution and repeatedly used in the *p*-CP conversion for five times.