



# Catalytic wet peroxide oxidation of phenol over $\text{Fe}_2\text{O}_3/\text{MCM-41}$ in a fixed bed reactor



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## ABSTRACT

Iron-containing (10 w/w%) MCM-41 catalysts were prepared and tested for catalytic wet peroxide oxidation (CWPO) of phenol aqueous solutions in a fixed bed reactor. First,  $\text{Fe}_2\text{O}_3/\text{MCM-41}$  catalysts were prepared by incipient wetness impregnation and characterized by using X-ray diffraction (XRD),  $\text{N}_2$  adsorption-desorption and X-ray photoelectron spectra (XPS), respectively. Second, the effect of temperature, catalyst bed height and feed flow rate on phenol mineralization, hydrogen peroxide and total organic carbon (TOC) conversions were studied to determine the optimum condition. Moreover, Fe leaching concentration was detected to study the stability of the  $\text{Fe}_2\text{O}_3/\text{MCM-41}$  catalyst. Finally, the evolution of intermediates was monitored to investigate the probable reaction mechanism of phenol oxidation over  $\text{Fe}_2\text{O}_3/\text{MCM-41}$  catalyst in the fixed bed reactor. The experimental results showed that the conversion of TOC reached 72.5% and few Fe (0.01 mg/L) was detected under optimum condition (namely, feed flow rate of 2.0 ml/min, temperature of 80 °C, catalyst bed height of 4 cm). The probable multistep reaction route for oxidative destruction of phenol over  $\text{Fe}_2\text{O}_3/\text{MCM-41}$  catalyst in a fixed bed reactor is based on hydroxyl radical reacting with phenol, resulted in aromatics such as catechol and hydroquinone, and p-benzoquinone, followed by evolution to carboxylic acids and finally completing oxidation to carbon dioxide and water. Few intermediate products were detected in the treated effluent when the catalyst bed height was higher than 2 cm.

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## 1. Introduction

Phenol, as one of the most important aromatic compounds, is a typical pollutant that mainly comes from petrochemical, textile mills, chemical pharmaceutical, refineries and many other industrial sectors [1,2]. Phenol wastewater is one of the most toxic pollutants, harmful to human health, leading to an increase in the demand of oxygen in water sources and releasing smelly taste in drinking water even at a low concentration. So it is usually taken as a model compound to study treatment of wastewater by various techniques [3]. Many techniques, such as biodegradation [4,5], electrochemical degradation [6], physical sorption [7] and the advanced oxidation Processes (AOPs) [8,9] have been used to treat the phenol wastewater.

Catalytic wet peroxide oxidation (CWPO) is one of the most environment-friendly and efficient advanced oxidation processes. It takes hydrogen peroxide as oxidant to degrade the phenol wastewater to carbon dioxide, water or some short-chain acids in presence of a catalyst under a mild condition [10]. Hydrogen

peroxide is a non-toxic reactant, it does not form any harmful byproducts, enhances the oxidation efficiency and decreases the harsh reaction conditions [11]. Usually, hydroxyl radicals were generated by the redox properties of the transition metals used as catalyst in presence of hydrogen peroxide [12]. CWPO takes advantage of decreasing the activation energy by using catalyst to make the reaction happen in a mild condition. In addition, hydrogen peroxide is employed as liquid oxidant in CWPO so as to overcome the gas–liquid mass transfer limitations and greatly improve the reaction efficiency. In the past decade, most of the researchers [13–16] have focused on the study of the CWPO processes of phenol carried out in a stirred tank reactor. Batch reactor exists some shortcomings such as high concentration of intermediate products and long contact time which may result in the lessen of longevity of the catalyst [17]. Some research data [1,18] indicate that the leaching of Fe ions from zeolite catalyst into the solution was strongly dependent on pH, which may affect badly on the longevity of catalyst as well as cause the secondary effluent contamination by the Fe ions. These drawbacks can be overcome by using a fixed bed reactor. Only few literatures reported the CWPO of phenolic solution in a fixed bed reactor. Botas et al. [19] reported a prominent catalytic performance of the  $\text{Fe}_2\text{O}_3/\text{SiO}_2$  and the

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Fe<sub>2</sub>O<sub>3</sub>/SBA-15 for the CWPO of phenolic solution in a fixed bed. The results show that activities above 50% in terms of TOC conversion and iron leaching below 15 mg/L was detected. Yan et al. [20] tested the catalytic performances of Fe-ZSM-5, which were used in a fixed bed reactor for the CWPO of phenolic solution. Few intermediate products were detected in the treated effluent by HPLC. Hardly any studies reported on the reaction mechanism of the CWPO of the phenol in a fixed bed reactor.

There are several references in the literature [21–23] focusing on the homogeneous and the heterogeneous catalysis in the CWPO of phenol wastewater. The main drawback of conventional CWPO is that it is badly affected by typical problems in homogeneous catalysis, such as additional water pollution and catalyst separation [24]. Fenton reaction, a typical homogeneous catalysis [25], uses hydrogen peroxide in the presence of Fe (II) salt to produce high fluxes of hydroxyl radicals with high oxidative power which can remove or degrade the recalcitrant organic pollutants in solution. The defect of this technology is the need of recovering the homogeneous catalyst [18] and the separation of Fe ions. The use of heterogeneous catalysts could be an alternative method of these problems. The heterogeneous catalysts, solids containing transition metal cations, can be easily recovered, regenerated, and reused [26].

Recent years, various kinds of materials like silica [19], pillared clays [27], activated carbons [28], Al<sub>2</sub>O<sub>3</sub> [29] and zeolites [18,30,31] have been used as supports to prepare the catalysts. Among these materials, zeolites is a promising catalyst supports due to their uniform porous structures, high specific surface area, as well as good hydrothermal and chemical stabilities. ZSM-5 as a typical microporous zeolites has a 10-ring interconnected channel system with a high Si/Al ratio [32]. However, the specific surface area of ZSM-5 is not large enough (about 300 m<sup>2</sup>/g), which may influence the mass transfer efficiency. Recently, mesoporous zeolites have proved to be promising heterogeneous catalysts in different applications. They are considered as excellent catalysts due to a large pore size that is supposed to enhance diffusion of reagents as compared to microporous materials [33]. MCM-41, a member of mesoporous zeolites M41S, possesses a hexagonally arranged uniformed pore structure with a broad spectrum of pore diameters between 15 and 100 Å [34]. High specific surface area (more than 800 m<sup>2</sup>/g), large pore volume and uniform pore size, which makes MCM-41 as a high quality material for a catalyst, catalyst support, or adsorbent [35] in the CWPO of phenol wastewater. In addition, MCM-41 is expected to enhance intraparticle diffusion when compared to microporous zeolite materials (such as ZSM-5) with its special characteristics such as higher surface area together with large pore size. Various of transition metal ions, such as Cu [34,36], Fe [37–39], Mn [40] and other transition or noble metal can be incorporated into the framework sites of MCM-41 or loaded on the surface of MCM-41. Iron containing mesoporous materials are of particular interest due to their unique catalytic properties in various reactions [41].

In our previous work [26], the performance of Fe-ZSM-5 (microporous material) catalyst for the CWPO of phenolic solution in a fixed bed reactor was evaluated, but the probable reaction mechanism didn't explore further (only qualitative analysis). The aim of our present work is devoted to study the efficiency of Fe<sub>2</sub>O<sub>3</sub>/MCM-41 (mesoporous material) catalyst prepared by incipient wetness impregnation for the CWPO of phenol aqueous solution in the fixed bed reactor. The feasibility of Fe<sub>2</sub>O<sub>3</sub>/MCM-41 catalyst for the degradation of aqueous phenolic solutions will be probed in the fixed bed reactor. The influence of the reaction temperature, catalyst bed height and feed flow rate will be discussed. In addition, the life-cycle of

Fe<sub>2</sub>O<sub>3</sub>/MCM-41 catalyst will be assessed for the treatment of phenolic aqueous solution to test the stability and reusability of the Fe<sub>2</sub>O<sub>3</sub>/MCM-41 catalyst. Then, the reaction mechanism of phenol wet catalytic oxidation over Fe<sub>2</sub>O<sub>3</sub>/MCM-41 will be studied by determining the concentrations of intermediates (qualitative analysis and quantitative analysis).

## 2. Experimental

### 2.1. Materials

Commercial MCM-41 zeolites (column; d = 4 mm, L = 2–3 mm) were obtained from Nankai University Catalyst Factory. Phenol was supplied by Guangzhou Chemical Reagent Factory. Hydrogen peroxide (H<sub>2</sub>O<sub>2</sub>, 30 wt% aqueous) and manganese dioxide were purchased from Shanghai Qiangshun Chemical Reagent Factory. Fe(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O was obtain from Tianjin Damao Chemical Reagent Factory. Sodium thiosulfate and potassium iodide were obtained from Tianjin Bodi chemical Co., Ltd. Benzoquinone, catechol and hydroquinone were purchased from Sinopharm Chemical Reagent Co., Ltd. were all used as standard samples for the experiment. All of the chemical reagents used in this research were analytical grade.

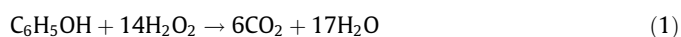
### 2.2. Preparation and characterization of Fe<sub>2</sub>O<sub>3</sub>/MCM-41 catalysts

Commercial MCM-41 zeolite particles (column; d = 4 mm, L = 2–3 mm) was used to prepare the Fe<sub>2</sub>O<sub>3</sub>/MCM-41 catalyst by wetness impregnation of with Fe(NO<sub>3</sub>)<sub>3</sub> salt solution. After impregnation, the particles were dried at 100 °C for 12 h. Then the particles were calcined in air with a heating rate of 1 °C/min until 550 °C in a muffle furnace for 6 h.

The crystallographic structures of the Fe<sub>2</sub>O<sub>3</sub>/MCM-41 catalyst were measured by X-ray diffraction analysis. XRD patterns were obtained with a PANalytical X'Pert Pro X-ray diffractometer using Cu Kα radiation (40 kV, 40 mA) and 2θ range from 1° to 10° and 5° to 60°. N<sub>2</sub> adsorption–desorption isotherms of catalyst sample were tested using an ASAP 2020 (Micromeritics Instrument Co., USA) at 77 K to get the BET specific surface area and total pore volume of the Fe<sub>2</sub>O<sub>3</sub>/MCM-41 catalyst and MCM-41 support. All of the samples were out-gassed on a Micromeritics Vacrep O61 Sample Degas System at 473 K for 4 h before measurement. X-ray photoelectron spectroscopy (XPS) spectra were recorded on a Kratos Axis Ultra (DLD) instrument and using an aluminium Kα radiation source operated at 15 kV and 10 mA.

### 2.3. Catalytic activity tests

The catalytic activity of Fe<sub>2</sub>O<sub>3</sub>/MCM-41 catalyst was tested by CWPO with phenol as a model pollutant in water in a fixed bed reactor made of a stainless steel tube (2 cm i.d., 10 cm length), operated at constant 80 °C of temperature. As shown in Fig. 1, the experimental device is used for the oxidation of phenol aqueous solution by means of catalytic wet peroxide oxidation. To enable a better distribution of the inlet aqueous solution inside the catalyst bed, the catalysts were placed in the catalytic packed bed between two beds of spherical inert glass particles (d = 2–3 mm). In the feed tank, the concentration of phenol is 1 g/L and the concentration of hydrogen peroxide is 5.1 g/L (stoichiometric amount for the total phenol oxidation according to reaction (1)). Phenol solution was transported to the up-flow fixed bed with a peristaltic pump. The fixed bed reactor was heated by water bath to keep temperature we desired. Here is the equation of the CWPO of phenol:



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