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Short communication

Catalytic wet peroxide oxidation of phenol wastewater over a novel Cu–ZSM-5 membrane catalyst

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ABSTRACT

A novel Cu–ZSM-5 membrane catalyst was prepared and characterized for catalytic wet peroxide oxidation (CWPO) of phenol wastewater in a continuous reactor. The Cu–ZSM-5 membrane catalyst was first prepared by the secondary growth process and incipient wetness impregnation method, and then characterized by thermal gravimetric (TG) analysis, N_2 adsorption–desorption, X-ray diffraction (XRD), scanning electron microscopy (SEM) and H_2-temperature programmed reduction (H_2-TPR), respectively. This catalyst exhibited an excellent catalytic performance (complete phenol conversion and TOC conversion about 65% without toxic quinones detected).

1. Introduction

Phenol wastewater discharged from industrial processes has become a great concern because it is resistant to biodegradation and toxic to animals and human beings [1]. Many researchers have focused on the degradation of phenolic pollutants by CWPO processes which using H_2O_2 as the green liquid oxidant. CWPO of phenol wastewater can be conducted at ambient conditions, and it can not only avoid gas–liquid mass transfer limitations, but also decrease the investment costs [2]. Heterogeneous catalysts used in CWPO processes can be easily separated, regenerated and reused and can overcome the conventional drawbacks of homogeneous catalysts. The introduction of transition metal oxides and their complexes such as Fe [3,4] and Cu [5,6] into numerous porous materials such as ZSM-5 [7,8], MCM-41 [9,10], SBA-15 [11,12] and activated carbon [3,6] can greatly improve the catalytic performance of CWPO. The catalysts based on copper oxides have showed higher activities when used in the CWPO of phenol wastewater [13]. Zeolite membranes as new catalyst supports have attracted more and more attention due to their uniform porous structures, unique surface properties, good mechanical strength, good chemical and hydrothermal stabilities, and it can be used directly into a continuous reactor [14]. Results on the CWPO of phenol in the presence of only Cu as active component at atmospheric pressure are reviewed by N.S. Inchaurrondo et al. [15]. Experiments were carried with all kinds of catalysts and under various reaction conditions such as catalyst load, temperature, reactant concentrations and pH values. All of these experiments were conducted in a bath reactor and complicated intermediate products with high concentration were detected. However, there is no literature report of the higher activity of Cu species loaded on the zeolite membrane support used for continuous CWPO of phenol wastewater.

In this study, we reported a novel type of catalytic material consisting of well crystalline copper oxide supported over a ZSM-5 membrane and studied its crystallographic structures and morphological information. The CWPO of phenol wastewater of high concentration (1000 mg/L) over this catalyst was evaluated in a continuous reactor, and the catalytic mechanism over the Cu–ZSM-5 membrane catalyst was proposed.

2. Experimental

2.1. Preparation of Cu–ZSM-5 membrane catalyst

Details of the synthetic procedure of paper-like stainless sintered steel fibers (PSSFs) and ZSM-5 membrane/PSSFs were reported in our previous paper [16]. In this study, the ZSM-5 membrane support with a Si/Al ratio of 80 was synthesized by the secondary growth method. Cu active component was loaded on the ZSM-5 membrane by means of incipient wetness impregnation. Cu ion (copper nitrate trihydrate obtained from Guangzhou Chemical Reagent Factory) concentration was adjusted to obtain 25 wt.% Cu loading on the catalyst. The sample was air dried at 100 °C for 12 h and calcined in air until 550 °C (6 h) using a ramp of temperature (1 °C/min).

2.2. Characterizations of Cu–ZSM-5 membrane catalyst

TG analysis of the uncalcined catalyst was investigated in nitrogen on a SDT Q600 analyzer (TA instrument Co., USA). N_2 adsorption–desorption isotherms of catalyst samples were tested using a Micromeritics Tristar II Surface Area and Porosity analyzer (Micromeritics Instrument Co., USA)

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at 77 K. The crystallographic structures of the ZSM-5 membrane and Cu–ZSM-5 membrane catalyst were studied by XRD patterns carried out on a PANalytical X'Pert Pro X-ray diffractometer. The textural and morphological information of the Cu–ZSM-5 membrane catalyst was characterized using FE-SEM on a Zeiss Merlin FE-SEM. H_2-TPR experiments were done in a Quantachrome Automated Chemisorption Analyzer.

2.3. Catalytic activity evaluation of Cu–ZSM-5 membrane catalyst in a continuous reactor

The CWPO experiments were carried out in a continuous reactor made of a stainless steel tube (20 mm i.d., 100 mm length), operating at a constant temperature of 80 °C under atmospheric pressure. The experimental set-up used for the CWPO of phenol is showed in Fig. S1. The prepared Cu–ZSM-5 membrane catalyst (catalyst bed height of 2 cm) was packed in the continuous reactor. The feed flow rate of the reactants is 2 mL/min and the concentration of reactants is a mixture of phenol solution, 1000 mg/L of phenol and 5100 mg/L of H_2O_2 (stoichiometric amount for the total phenol oxidation according to reaction (1)). The phenol solution with a concentration of 1000 mg/L was prepared by accurately weighing 1.0000 g phenol solid (analytically pure) and dissolving with 1 L water in a brown volumetric flask.

$$C_6H_5OH + 14H_2O_2 \rightarrow 6CO_2 + 17H_2O \tag{1}$$

The H_2O_2 concentration was firstly determined by iodometric titration using a 0.02 mol/L sodium thiosulfate solution. Phenol concentration was measured by means of an HPLC Chromatograph (Agilent 1260 infinity) equipped with an Agilent HC-C18(2) column and a UV detector adjusted at 210 nm. Total organic carbon (TOC) concentration of the samples was measured using a Liqui TOC (Elementar, Germany). Cu leaching concentration in the treated effluent was tested by an atomic absorption spectrophotometer (AAS, HITACHI Z-2300).

3. Results and discussion

3.1. Characterizations

TGA and DTA experiments of the uncalcined Cu–ZSM-5 membrane catalyst were firstly conducted, and the results were shown in Fig. 1. As can be seen in Fig. 1, there are three main weight losses during the decomposition processes. The first weight loss from 50 °C to 150 °C was due to desorption of physically absorbed water. The second weight loss from 150 °C to 200 °C was resulted from the formation of $Cu_4(NO_3)_2(OH)_6$, which could be described as reaction (2). And the last weight loss from 220 °C to 300 °C was induced by the decomposition of $Cu_4(NO_3)_2(OH)_6$, which could be described as reaction (3) [17]. The catalyst showed a good thermal stability because no obvious peaks were detected when the temperature increased from 600 to 800 °C. All of the Cu species were transformed into CuO after 550 °C. Therefore, calcination temperature at 550 was chosen in order to obtain well crystalline CuO particles.

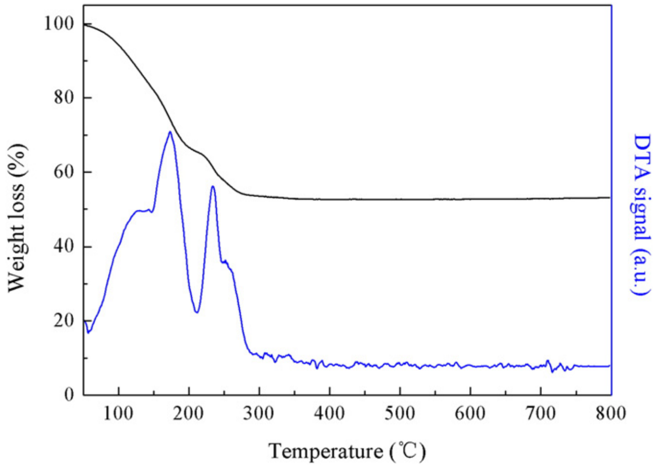

Fig. 1. TGA profiles of the uncalcined Cu–ZSM-5 membrane catalyst.

$$4Cu(NO_3)_2 \cdot 3H_2O \rightarrow Cu_4(NO_3)_2(OH)_6 + 6HNO_3 + 6H_2O \tag{2}$$

$$2Cu_4(NO_3)_2(OH)_6 \rightarrow 8CuO + 4NO_2 + 6H_2O + O_2 \tag{3}$$

Specific surface areas and porosity properties of ZSM-5 membrane and Cu–ZSM-5 membrane catalyst were characterized by N_2 adsorption–desorption. The N_2 adsorption–desorption isotherms of the catalysts were displayed in Fig. S2, and the BET surface areas and pore properties were summarized in Table 1. Fig. S2 shows that the volume adsorbed increases with increasing relative pressures for all isotherms which is due to the volume filling of micropores in the ZSM-5 membrane. Both of the catalysts were fit for type I isotherms which were given by microporous solids [18]. As listed in Table 1, the BET specific surface area and total pore volume (V_t) of the Cu–ZSM-5 membrane catalyst were 147.5 m^2/g and 0.0805 cm^3/g, respectively. The ZSM-5 membrane catalyst exhibited higher BET specific surface area (215.7 m^2/g) and total pore volume (0.1059 cm^3/g) than the Cu–ZSM-5 membrane and the volumes of micropores (V_{micro}) decreased from 0.05651 cm^3/g to 0.05198 cm^3/g. The decreases of volume may result from the blockage of the Cu–ZSM-5 membrane catalyst. The ZSM-5 membrane with a higher Si/Al ratio of 80 exhibited higher S_{BET} than the former ZSM-5 membrane (Si/Al = 62.5, S_{BET} = 145 m^2/g) [16]. It can be concluded that the introduction of CuO active component will decrease the BET surface area and total volume of ZSM-5.

The crystallographic structures of the ZSM-5 membrane support and Cu–ZSM-5 membrane catalyst samples were studied by XRD patterns, which were shown in Fig. 2. Both of the XRD patterns show the diffraction peaks at the ranges of $2\theta = 7–9°$ and $2\theta = 23–25°$, matching well with the standard phase of ZSM-5 zeolite [19]. For the CuO loaded ZSM-5 membrane catalyst, two strong peaks of copper oxide at $2\theta = 35.5°$ and $2\theta = 38.7°$ are detected. The size of the CuO crystallite (about 28 nm) was obtained from the processed results of the XRD analysis. The structure of the ZSM-5 zeolite remained intact after the modification treatment, whereas a decrease of the intensity of ZSM-5 zeolite diffraction peaks was observed compared with the ZSM-5 membrane, which could result from the higher X-ray absorption coefficient of copper compounds. It can be concluded that CuO active component with a well crystalline membrane was successfully loaded on the ZSM-5 membrane support.

Morphology and structure of the synthesized materials were investigated by FE-SEM. Fig. 3 shows the FE-SEM images of the ZSM-5 membrane support and Cu–ZSM-5 membrane catalyst. Fig. 3(a) clearly shows that the junctures of stainless steel fibers are sintered together to form a three-dimension network structure. Fig. 3(b) shows that the continuous ZSM-5 zeolite membrane (about 5 μm) with a good crystal form covered on the surface of stainless steel fiber is thicker than the ZSM-5 membrane with a Si/Al ratio of 62.5 [16]. As can be seen in Fig. 3(c) and (d), CuO particles were loaded on the surface of the ZSM-5 zeolite membrane and stocked part of the space of PSSFs. Part of the space of the ZSM-5 zeolite membrane was blocked and embedded by the CuO particles and thus results in the decreases of the three dimension structure of the ZSM-5/PSSFs. The FE-SEM images indicate that

Table 1
Physiochemical properties of the catalysts.

Sample	S_{BET} (m^2/g)	V_t (cm^3/g)	V_{micro} (cm^3/g)	V_{meso} (cm^3/g)
ZSM-5 membrane	215.7	0.1059	0.05651	0.01676
Cu–ZSM-5 membrane	147.5	0.0805	0.05198	0.01881