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Cu-MFI zeolite supported on paper-like sintered stainless fiber for catalytic wet peroxide oxidation of phenol in a batch reactor

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ABSTRACT

Structured copper-containing MFI-type (Cu-MFI) zeolite catalysts on paper-like sintered stainless fiber (PSSF) were prepared by a secondary hydrothermal synthesis method and resulting in Cu-MFI coating with good relative crystallinity (80.7%), high BET surface area (237.5 m^2/g) and uniform pore size distribution (2–3 nm). The influence of synthesis temperature (120–180 °C) and crystalline time (6–48 h) on the relative crystallinity and thickness of the MFI coating were investigated by XRD and SEM showing the adjustable coating thickness of SiCuMFI zeolite (1–7 μm). Both framework and non-framework (as CuO phase) Cu species were identified for the prepared catalysts by XPS and H_2-TPR. Specifically, the framework Cu species were confirmed by FT-IR, Raman and UV-vis spectroscopic analyses, showing the effectiveness of the current method for promoting the incorporation of Cu in the MFI framework. A new impeller was designed to host the developed structured catalysts, which allowed the facile use of the catalyst for the practical application in a batch reactor for water/wastewater treatment. Catalytic tests (using phenol as the model pollutant) showed the outstanding catalytic activity of the developed catalysts (99% conversion after 40 min) with negligible Cu leaching (lower than 1 mg/L).

1. Introduction

Cu species as active catalyst components were widely used in various field such as the catalytic decomposition of NO_x [1–5], the synthesis of methanol [6–8], the methanol steam reforming [9], the desulfurization of diesel fuel [10], and the oxidation carbonylation of methanol to dimethyl carbonate [11,12]. In recent years, much attention has been given to the practical use of Cu-based catalysts for environmental catalysis. For example, Cu supported on ZSM-5 catalysts have been recognized as one of the most active catalysts for NOx decomposition [4,13,14]. Cu-based catalysts also showed high catalytic active when used in the degradation of organics (e.g. phenol, methylphenol and nitrophenols) in wastewater, especially, combined with the catalytic wet peroxide oxidation processes [15,16]. Compared with Fe catalysts, the Cu species showed higher activity when used in the CWPO process of wastewater [17]. However, Cu as the active species was very unstable and prone to leaching, e.g. > 100 mg/L Cu species was leached into the solution in treatment of phenol wastewater [18].

Framework materials (e.g. zeolites such as MFI [19,20]) are ideal support to disperse Cu species for catalytic applications due to the high chemical and thermal stability and well-developed pore networks. To support Cu species on framework materials, post-synthetic preparation methods of incipient wetness impregnation and ion exchange tended to produce non-uniform Cu species across the framework, and hence leading to the catalyst with poor activity [21] and leaching problems [22]. On the contrary, direct hydrothermal synthesis of framework materials with Cu species was able to incorporate Cu species into the framework promoting the dispersion of active sites and preventing the leaching of the active sites from the porous supports.

Structured catalysts and reactors (e.g. structured foams [23], compact multifunctional reactors [24] and PSSF) have been well-received by the community as the main enablers for transferring bulk catalysts to applications in practical settings. Specifically, the process based on structured technologies does not require the separation of catalysts from the reaction media, significantly reducing the associated operation time and cost. The PSSF, with a thickness of 1–2 mm, has three dimension structures with high porosity and relevant features of stainless steel. The PSSF has very good flexibility and can be easily shaped according to the type of a reactor. Previously, we have demonstrated the use of PSSF as the structured support (e.g. for microfibers and zeolites) for applications in adsorption and catalysis [25–28].

Although many researchers have focused on the preparation of metal containing zeolites for various applications, there were few literatures concentrated in the hydrothermal synthesis of Cu containing zeolite catalysts, especially the Cu doped MFI zeolite coated on the PSSF which can combine the advantages of PSSF and MFI structure and can

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be used in different reactor with high efficiency. Meanwhile, the influence of metal doped content, synthesis conditions of the catalysts, the phase information of the doped active component and the catalytic activity need further investigation. This catalyst may deal with the problem of high leaching concentration of the Cu loading catalysts when used in the water treatment.

The aim of this study is to (a) prepare the Cu doped MFI-type zeolite catalysts coated on PSSF, (b) investigate the catalytic activity and the influences of doped Cu on the framework of the MFI structure by systematically characterization of the catalysts, and (c) develop a batch reactor to evaluate the zeolite coating catalysts by means of CWPO process.

2. Experimental

2.1. Materials and chemicals

Stainless steel fibers (average diameter about 6.5 μm, average length of 3 mm) were purchased from Huitong advanced material company (China). Tetraethoxysilane (TEOS, > 99%), phenol and copper nitrate trihydrate were obtained from Guangzhou Chemical Reagent Factory. Hydrogen peroxide (H_2O_2, 30 wt% aqueous) was obtained from Jiangsu Qiangsheng Chemical Co., Ltd. Tetrapropylammonium hydroxide (TPAOH, 25 wt% aqueous) was purchased from Sigma-Aldrich. Ethanol (C_2H_5OH, > 99.8%), ammonia water (NH_3, 25–28 wt% aqueous) were all purchased from Sinopharm Chemical reagent Co., Ltd. Deionized water was used in all synthesis.

2.2. Preparation of Cu-MFI zeolite supported on PSSF

2.2.1. Preparation of PSSF

Details of the preparation process of PSSF were depicted in the Supplementary materials. In general, PSSF supports (round sheets with diameter of 15 cm and thickness of 2 mm) were prepared by wet lay-up papermaking process and then sintered at 1050 °C under N_2 atmosphere (flow rate of 250 mL/min). The synthesized PSSF supports were washed two times with NH_3 aqueous solution (0.1 mol/L) and then dried in air.

2.2.2. Synthesis of SiCuMFI zeolite supported on PSSFs catalysts

A secondary growth method was employed to prepare the Cu-MFI coating on PSSFs supports, which included the synthesis of silicalite-1 seeds, the adsorption of silicalite-1 seeds on PSSF and the secondary growth of the seeds to transform the seeds into the Cu-MFI coating on PSSF. Silicalite-1 seeds were obtained by a hydrothermal synthesis (at 100 °C for 24 h) using the synthesis solution with the composition of 9TPAOH:25TEOS:500H_2O:100C_2H_5OH. The pretreated PSSF supports (length = 60 mm, width = 40 mm, thickness = 2 mm) were coated with silicalite-1 seeds and dried under air at 100 °C.

To prepare the synthesis solution, TEOS was added dropwise into the vigorously stirring TPAOH solution. $Cu(NO_3)_3$ solution was then added into the mixture to form a light-blue solution which was vigorously stirred for 24 h before the secondary growth synthesis. The amount of $Cu(NO_3)_3$ was varied to prepare Cu-MFI coating with different Si to Cu ratio, shown in Table 1.

The seeded PSSFs were immersed vertically in a 200 mL Teflon lined autoclave with the secondary synthesis solution and treated hydrothermally in an oven at 150 °C for 48 h. After the synthesis, the sample was washed with deionized water, air dried (at 100 °C for 12 h) and calcined (in air at 550 °C for 6 h) to remove the TPAOH. The MFI zeolite supported on PSSFs (SiMFI/PSSF, without Cu species) was also prepared as the reference catalyst. The synthesis temperature (120, 150 and 180 °C) and time (6, 12, 24 and 48 h) in the secondary growth synthesis were studied to understand the influence of the synthesis condition.

Table 1
Molar ratio of the synthesis solution for the secondary growth synthesis and the notation of catalysts.

Name	Si/Cu Ratio	TEOS	TPAOH	$Cu(NO_3)_2$	H_2O
SiMFI/PSSF	Without Cu	1	0.112	0	111
SiCuMFI-80	Si/Cu = 80	1	0.112	0.0125	111
SiCuMFI-40	Si/Cu = 40	1	0.112	0.025	111
SiCuMFI-20	Si/Cu = 20	1	0.112	0.05	111
SiCuMFI-10	Si/Cu = 10	1	0.112	0.1	111

2.3. Characterization of the developed materials

X-ray diffraction (XRD) patterns of the materials were obtained using a PANalytical X'Pert Pro X-ray diffractometer with Cu Kα radiation (40 kV and 40 mA). The diffraction 2θ range was from 5° to 60° with a resolution of 0.02°. The relative crystallinity (or percent crystallinity) of zeolite Cu-MFI coating was calculated by using a standard Integrated Peak Area Method [23].

The textural and morphological information of the materials were characterized using an S-3700N scanning electronic microscopy (SEM). The samples were coated with Au films before the SEM analysis. The energy dispersive spectroscopy (Bruker, Quantax400) for element mapping (EDS mapping) was applied to analyze the dispersion of Si, Cu in the MFI zeolite coating.

N_2 adsorption–desorption isotherms of the materials were obtained using a Micromeritics Tristar II Surface Area and Porosity (3020 version 3.02, Micromeritics Instrument Co., USA) at −196 °C. Before the analysis, materials were out-gassed on a Micromeritics Vacrep O61 Sample Degas System at 250 °C for 6 h to clean the surface. Brunauer-Emmett-Teller (BET) method was used to determine the specific surface areas (S_{BET}) using adsorption branches at the relative pressure range of 0.06–0.3. The micropore surface area ($S_{micropore}$) and volume ($V_{micropore}$) was calculated using the t-plot method. And the adsorption average pore diameter was calculated by 4V/A (where V is the total volume and A is the BET surface area).

Fourier transform infrared (FT-IR) spectroscopy was performed using a Perkin-Elmer 100 spectrometer with a resolution of 4 cm^{-1} in the range from 400 to 2000 cm^{-1} at room temperature. Materials (1 wt %) were diluted with KBr to prepare pellets for the FT-IR analysis. Diffuse-reflectance spectra of materials were collected using a Shimadzu UV-2450 UV-vis spectrophotometer in a 250 nm–800 nm range. Raman spectra of materials were recorded using a Lab RAM Aramis Raman Spectrometer (HORIBA JOBIN YVON, France) with the spectrum range from 200 to 1600 cm^{-1} (632.81 nm wavelength laser was used as the spectrum source).

X-ray photoelectron spectroscopy (XPS) was performed on a Kratos Axis Ultra (DLD) spectrometer with an Al Kα (1486.6 eV) radiation source operated at 15 kV and 10 mA. The binding energy (B.E.) of C1s peak at 284.6 eV was taken as a reference.

Temperature-programmed hydrogen reduction experiments (H_2-TPR) were carried out in a Quantachrome Automated Chemisorption Analyzer with a thermal conductivity detector (TCD). To eliminate contaminants, catalyst samples were pre-treated at 300 °C under a Helium atmosphere (flow rate = 30 mL/min) and then cool down to 50 °C. Then, a gas mixture of H_2 (10 vol%)/Ar flow (flow rate = 30 mL/min) was passed over the sample, followed by a temperature ramp of 10 °C/min from 50 to 700 °C for the reduction process. The TCD signals of the effluent gas were recorded for quantifying the reduction ability.

2.4. Catalytic wet peroxide oxidation of phenol wastewater over Cu-MFI/PSSF catalysts

As depicted in Fig. 1, a new batch reactor was designed to evaluate the catalytic activity of the Cu-MFI zeolite coating catalysts. The designed batch reactor contains two main parts: a glass flask (1000 mL)