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Preparation of metallophthalocyanine functionalized magnetic silica nanotubes and its application in ultrasound-assisted oxidative desulfurization of benzothiophene

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ABSTRACT

In this study, the preparation and catalytic application of tetra-substituted carboxyl iron phthalocyanine (FeC_4Pc)-loading magnetic silica nanotubes (MSNTs) in oxidative desulfurization (ODS) of benzothiophene was investigated. The resulting materials FeC_4Pc-MSNTs integrate the advantages of silica nanotubes and superparamagnetic characteristics, which exhibited excellent catalytic activity and reusability. Under the best operating condition for the catalytic oxidative desulfurization, the sulfur content in model oil was reduced from 600 ppm to 35 ppm with 94% of total sulfur. Our work herein reveals that the surface functionalized MSNTs will be a promising platform as catalyst carriers.

1. Introduction

Nowadays, increasing attention has been paid to the environment issue caused by sulfur compounds in transportation fuels which is the main source of SO_x in air [1]. Oxidative desulfurization (ODS), an alternative or complementary technology to hydrodesulfurization for deep desulfurization, has been widely studied in recent years [2]. Different supported catalysts compound with H_2O_2 have been used in the oxidation of the organosulfur compounds, such as H_2O_2/Mo/γ-Al_2O_3 [3], H_2O_2/Ti-HMS [4], and H_2O_2/Fe/activated carbon [5]. Due to the bulky size of some refractory sulfur compounds (eg.: benzothiophene, dibenzothiophene and their alkyl-derivatives), materials with relatively lager porous structure as supports are thought to be best suited for ODS than conventional microporous solids. With the development of nanotechnology, nanomaterials as promising supported materials have found increasing applications in modern industry applications. Among them, silica nanotubes (SNTs) are attracting a great deal of attention due to their fundamental significance and potential applications in various areas.

SNTs have attracted special interest because of their easy surface functionalization, colloidal suspension formation, and hydrophilic nature [6]. The unique, hollow inner voids of nanotubes allow for filling with species ranging from large polymers to small molecules to meet different requirement [7,8]. And by combining the attractive tubular structure of silica nanotubes with magnetic properties, magnetic silica nanotubes (MSNTs) not only have all the advantages of silica nanotubes, but also have the potential to be separated from solution by external magnetic field [9,10]. It is well known that metallophthalocyanines have been used as an efficient biomimetic catalysts for the oxidation, reduction and other reactions because of their chemical and thermal stabilities and also their rather cheap and facile preparation in large scale [11–14]. According to our previous work [15], the multifunctional nanotubes supported metallophthalocyanine material was expected to be a useful catalyst for ODS process. However, the reports on the applications of these MSNTs in catalytic chemistry are rare.

In this work, the direct preparation of surface amino-functionalized MSNTs, the covalent attachment of FeC_4Pc on the surface of amino-functionalized MSNTs and its application as a new catalyst for the ultrasound-assisted ODS with the viewpoint of green chemistry is reported. The physicochemical properties, catalytic performance and reusability of FeC_4Pc-MSNTs were studied. It reveals that FeC_4Pc supported on MSNTs

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exhibits a high ODS activity because the unique silica surface chemistry of MSNTs provided a benign microenvironment for catalytic reaction.

2. Experimental

2.1. Materials

A commercially available AAO membrane with a diameter of 47 mm and a quoted pore diameter of 200 nm was purchased from Whatman. Tetraethoxysilane (TEOS), 3-aminopropyltriethoxysilane (APTEOS) and ethyl-[3-(dimethylamino) propyl]–carbodiimide hydrochloride(EDC) were purchased from Aldrich. *N*-hydroxysuccinimide (NHS) was purchased from Sigma. FeC_4Pc were obtained from Sigma. Hydrogen peroxide solution was prepared by dilution of 30% aqueous solution and standardized by titration with the standard solution of potassium permanganate. All other chemicals were of analytical-reagent grade and used without further purification.

2.2. Synthesis

2.2.1. Preparation of amino modified MSNTs

The surface amino modified MSNTs(NH_2-MSNTs) were prepared according to the literature [16–18]. Firstly, the AAO membrane was immersed in a mixture solution composed of APTEOS, ethanol, sodium acetate and water for 10 min and heated in vacuum at 130 °C for 2 h. After a brief mechanical polishing and rinsing, the membrane was modified with magnetite nanoparticles by coprecipitating Fe^{3+} and Fe^{2+} under an N_2 stream. Finally, the magnetite-modified AAO membrane was immersed in a pre-made hydrolyzed silica solution for 1 min at 4 °C. This pre-made solution was prepared by mixing TEOS, APTEOS, ethanol, H_2O and HCl and stirred at room temperature. The AAO membrane was then dried at 90 °C under vacuum for 2 h. After dissolving completely the alumina membrane in NaOH (0.1 M), the resulting NH_2-MSNTs were collected by centrifugation, washed with deionized water and ethanol several times.

2.2.2. Preparation of FeC_4Pc-MSNTs

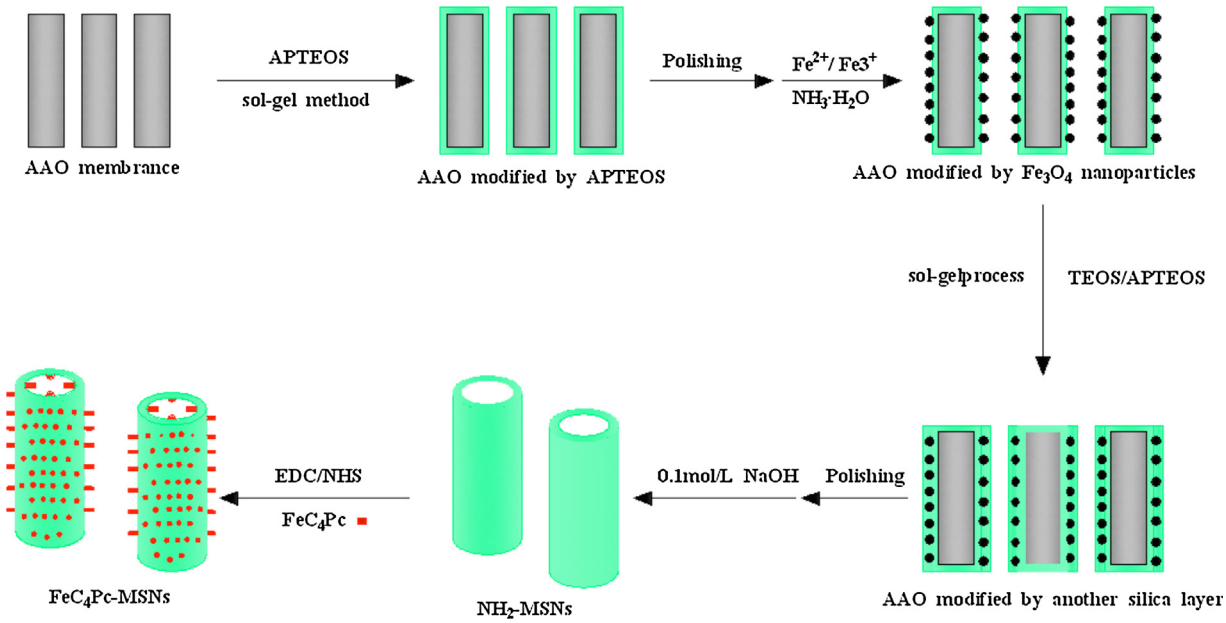
To covalently bind FeC_4Pc to the NH_2-MSNTs, 3 mg FeC_4Pc was firstly added to 2 mL anhydrous dimethylformamide by stirring for 10 min. After appropriate amount of EDC and NHS were added into the FeC_4Pc solution, stirring was continued for another 20 min. 0.2 g NH_2-MSNTs was then added. The sample solution was stirred at room temperature for 2 h to allow the immobilization equilibrium. Thereafter, the immobilized FeC_4Pc was separated from the solution by centrifugation and washing with water several times to remove the desorbed FeC_4Pc completely.

2.3. Characterization

Scanning electron microscope (SEM) and X-ray energy dispersion spectroscope (EDS) images of the MSNTs were taken on a LEO 1530 SEM equipped with ISIS 300 INCA energy and INCA crystal system (Oxford Instrumental Pte. Ltd.). A Tecnai F30 transmission electron microscope (TEM) was used to obtain TEM micrographs of MSNTs. Magnetic characterization of MSNTs was performed by a superconducting quantum interference device (Magnetic Property Measurement System XL-7, Quantum Design). A Hitachi F-4500 fluorescence spectrofluorimeter was adopted to record the steady-state fluorescence spectra and make the fluorescence measurements. A Beckman DU-7400 UV–vis diode array spectrophotometer was used to record absorption spectra.

2.4. Catalytic activities

The catalytic oxidative desulfurization experiments were conducted in a flask using a model oil(MO) consisting benzothiophene (BT) and octane with initial sulfur contents of 600 mg/L. A typical experiment was performed as follows: In a round bottom flask with a heated circulating bath, 10 mL of MO was mixed with FeC_4Pc-MSNTs (or FeC_4Pc), and hydrogen peroxide. The mixture was irradiated using ultrasound for a specific time at a given temperature. After the reaction, the oxidized MO was extracted by extraction solvent and the oil layers were collected and analyzed for sulfur content by gas chromatography with flame photometric.



Scheme 1. Schematic illustration of the synthesis of FeC_4Pc-MSNTs.