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Metallophthalocyanine functionalized magnetic mesoporous silica nanoparticles and its application in ultrasound-assisted oxidation of benzothiophene

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In this study, the preparation and catalytic application of tetra-substituted carboxyl iron phthalocyanine (FeC_4Pc)-loading core-shell-structured mesoporous silica nanoparticles (MSNPs) in oxidative desulfurization (ODS) of fuel oil with the assist of ultrasound were investigated. The morphology and the mesoporous feature of the composite were characterized by TEM, SEM and BET techniques. Linking FeC_4Pc to the mesoporous silica shell has been verified to play a positive role in UAOD process. Meanwhile, The influences of ultrasound power, reaction temperature, H_2O_2:oil molar ratio and the reuse of catalyst on the catalytic oxidation desulfurization were studied. It reveals that the resulting materials FeC_4Pc-MSNPs integrate the advantages of mesoporous silica nanoparticles and superparamagnetic characteristics, which exhibited excellent catalytic activity and reusability in UAOD process. Under the optimized conditions: (ultrasonic time 30 min, temperature 60 °C, catalyst dosage of 20 g/L, H_2O_2/sulfur molar ratio of 20) for the catalytic ODS, the sulfur content in model diesel fuel was reduced from 600 ppm to 33 ppm with 94.5% of total sulfur.

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1. Introduction

In the past two decades, rapid technological advancement and increasing world population have led to a markedly increase in fuel consumption. Sulfur compounds present in fuels not only can cause serious environmental pollution but also can lead to severe corrosion of reactors and equipment in oil processing. Moreover, sulfur is also a well-known poison for catalytic processes in petroleum processing. According to stringent environmental legislation, US Environmental Protection Agency (EPA) and European Union (EU) stated that the sulfur level in commercial fuel (diesel and gasoline) should be less than 10 mg/L by 2013 [1,2]. With the growing awareness of environmental protection, the deep removal of sulfur from transportation fuels, especially gasoline and diesel, has become increasingly important.

In order to produce low-sulfur fuels, attention has been drawn to technologies such as hydrodesulfurization (HDS), liquid/liquid extraction, biocatalytic-desulfurization and oxidative desulfurization [1–3]. Conventional reducing sulfur levels of transportation fuels rely on the HDS processes, which are highly efficient for the removal of thiols and sulfides [4]. However, the process requires high hydrogen pressure, high operating temperature, large reactors and a long residence time, which mean high operating costs [5]. In addition, aromatic sulfur compounds such as benzothiophene (BT), dibenzothiophene (DBT) and other dibenzothiophene derivatives are resistant to HDS treatment and require more severe reaction conditions [6,7].

Oxidative desulfurization (ODS) is one of the most promising technologies for deep desulfurization of fuel oil. In comparison to HDS, this method has several advantages since it could be carried out under mild conditions (low pressure and temperature), provides high selectivity and does not utilize expensive hydrogen in its operations [8]. Various oxidation systems with several homogenous and heterogeneous catalysts such as organic acids [9], polyoxometalates [10], metal oxide supported on alumina or silica [11–15], and other molecular sieves [16] have been considered to enhance oxidative activity of the oxidizing agents. Among these oxidation systems, H_2O_2/metalloporphyrins oxidative system has been investigated in some research groups due to its high catalytic activity in oxidation of sulfur compounds [17–19]. Zhou et al. studied the direct oxidative removal of DBT using different iron

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phthalocyanines catalysts [17]. The results show that the catalytic activity of these phthalocyanines decreases in the order of $FePc(NO_2)_4 > FePc(NO_2)_3NH_2 > FePc(NH_2)_4$, and the conversion of DBT in decalin reached 98.7 wt.% at 100 °C and 0.3 MPa of initial pressure using 1 wt.% of $FePc(NO_2)_4$ over the whole solution, after 2 h treatment. Combined adsorption process, the lowest sulfur content in the model fuel could be decreased from 500 μg/g to less than 4 μg/g. Pires et al. also obtained an excellent sulfur removal efficiency of different diesel fuels in the H_2O_2/manganese porphyrin complexes oxidative system [19]. They reported that after treated with catalytic oxidation using hydrogen peroxide and [Mn(TDCPP)Cl] as catalyst, the removal efficiency of sulfur for different diesel fuels with various sulfur content can reach or exceed 99% at ambient pressure and temperature. However, homogeneous catalysts are difficult to be separated from the reaction products, which limited their recyclability.

Despite the advantages of ODS development, major limitations are low efficiency of the process, extended reaction time and excessive decomposition of hydrogen peroxide. To further improve desulfurization efficiency, an innovative technology called ultrasound-assisted oxidative desulfurization (UAOD) was introduced. A UAOD process usually combines phase transfer catalysis, transition metal catalyst and ultrasound that provides selective removal of organic sulfur compounds by combining with selective oxidation, solvent extraction and/or solid adsorption [20]. It is well known that ultrasonication has a remarkable influence on increasing the rate and/or yield of chemical homogenous and heterogeneous reaction. The sonication effect is based on cavitation which is comprised of formation, growth and implosive collapse of the microbubbles that creates an extreme local temperature and pressure at the center of the collapsing bubbles. As a result, a huge amount of energy is released which can lead to simple formation of active intermediates and subsequently promotion of the rate and/or yield of the reaction directly [21–24]. There are several studies reported on UAOD, which utilize different oxidation systems such as H_2O_2-acetic acid [25], H_2O_2-phosphotungstic acid [12,13], and H_2O_2-metal oxide [14,15]. But the research about H_2O_2/metalloporphyrins oxidative system on the oxidative removal of sulfur-containing compounds under ultrasound irradiation is rare.

It is well known that metallophthalocyanines have been widely used as an efficient biomimetic catalysts for the oxidation, reduction and other reactions [17–19]. However, the long contact time and separation problem hinder its industrial application. According to our previous work [26], composite nanomaterials with large surface area may provide a potential solution to the above problems. Mesoporous silica nanoparticles (MSNPs) are drawing a lot of attention owing to their uniform pore size, large surface area, high accessible pore volume, and ease of chemical modification. By combining the attractive mesoporous structure of silica nanoparticles with magnetic properties, magnetic MSNPs not only have all the advantages of silica nanoparticles, but also have the potential to be separated from solution by an external magnetic field. The porous structure of MSNPs not only permits the accommodation of a large quantity of metallophthalocyanines, but also helps to provide a benign microenvironment for the catalytic reaction. Supporting metallophthalocyanines on MSNPs can increase the active surface area of catalysts in metallophthalocyanines-catalyzed reactions, and make it easy to separate them by filtration, centrifugation or magnetic separation. In addition, solid particles can homogenize the distribution of ultrasound field and result in a better sonochemical effect by providing more active nucleation sites for cavitation bubbles [27–29]. However, to the best of our knowledge, any literature about the applications of these magnetic MSNPs supported FeC_4Pc in UAOD process has not been reported.

In this study, the preparation of FeC_4Pc modified magnetic MSNPs and its application as a new catalyst for ultrasonic assisted ODS with the viewpoint of green chemistry is reported. The physicochemical properties, influencing factors on the oxidative performance of BT and reusability of FeC_4Pc-MSNPs were studied. It reveals that FeC_4Pc supported on magnetic MSNPs exhibits a high ODS activity, because the violent movement of solid particles under ultrasound can greatly boost the mass transfer in the reaction. On the other hand MSNPs provided a benign microenvironment for catalytic reaction due to the unique silica surface chemistry. The study provides a new catalytic oxidative system combining H_2O_2 with supported FeC_4Pc and ultrasound irradiation for the removal of sulfur.

2. Experimental

2.1. Materials

Oleic acid, oleylamine, benzyl alcohol, tetraethoxysilane (TEOS), 3-aminopropyl –triethoxysilane (APTES) and ethyl-[3-(dimethylamino) propyl]-carbodiimide hydrochloride (EDC) were purchased from Aldrich Chemical Co. N-hydroxysuccinimide (NHS) were purchased from Sigma. Iron(III) acetylacetonate ($Fe(acac)_3$) was obtained from Strem Chemical Inc. Brij 56 was purchased from Alfa Aesar. FeC_4Pc was 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. Catalyst preparation

2.2.1. Synthesis of Fe_3O_4 nanoparticles

The magnetic particles were prepared through a solvothermal reaction [30]. Briefly, 0.53 g of $Fe(acac)_3$, 2.3 mL oleic acid and 2.3 mL oleylamine were added to 15 mL of benzyl alcohol under magnetic stirring. The obtained homogeneous yellow solution was transferred to a Teflon-lined stainless-steel autoclave and sealed to heat at 180 °C. After reacting for 10 h, the autoclave was cooled to room temperature. The obtained black magnetite particles were washed with ethanol three times, and then redispersed in 13.5 mL cyclohexane for further use.

2.2.2. Synthesis of $Fe_3O_4@SiO_2$

The nonporous silica layer was coated on the Fe_3O_4 nanoparticles by a reverse micelle method. In a typical procedure, 2 g of Brij56, 1.2 mL of the above cyclohexane suspension of Fe_3O_4 nanoparticles, 0.12 mL H_2O and 0.45 mL concentrated ammonia were added to 8.5 mL cyclohexane. After stirring for 30 min, 1.2 mL of TEOS was added. The reaction mixture was further stirred for 8 h at 50 °C in a water bath. The particles were separated and washed with ethanol for a few times. The obtained $Fe_3O_4@SiO_2$ magnetic nanoparticles were stored for further use.

2.2.3. Synthesis of FeC_4Pc-MSNPs

FeC_4Pc-APTES conjugate was prepared in advance. In a flask, 3 mg of FeC_4Pc and 15 uL of APTES were mixed in 2.5 mL of DMSO. Next, 4.5 mg of EDC and 3.0 mg of NHS were added into the mixture and stirred for 24 h at room temperature. The obtained solution was directly used without further treatment. The FeC_4Pc functionalized magnetic MSNPs (FeC_4Pc-MSNPs) were prepared by a modified Stöber sol–gel process [31]. Typically, 0.3 g $Fe_3O_4@SiO_2$ nanoparticles, 0.26 g CTAB, 0.75 mL concentrated ammonia and 37.5 mL ethanol were added to 81 mL H_2O. After being ultrasonicated for 10 min, 1.5 mL of the FeC_4Pc-APTES solution and

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