Construction of polyoxometallate-based organic-inorganic hybrid nanowires for efficient oxidative desulfurization

Huawei Yang[a,b], Bin Jiang[a], Yongli Sun[a], Xiaowei Tantai[a], Xiaoming Xiao[a], Jingyuan Wang[a], Luhong Zhang[a,*]

[a] School of Chemical Engineering and Technology, Tianjin University, Tianjin 300072, People's Republic of China
[b] School of Chemistry and Materials Science, Ludong University, Yantai 264025, People's Republic of China

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ABSTRACT

In this work, novel POMs-based organic-inorganic hybrid nanowires were prepared facilely and proposed as catalysts for oxidative desulfurization (ODS) of fuel with hydrogen peroxide (H_2O_2, 30 wt%) as an oxidant. The preparation was based on the ionic self-assembly between centrosymmetric organic bivalent cations and poly-molybdate anions without using any template agents or toxic organic solvents. The as-prepared nanowire was characterized by different techniques, which verified the formation of uniform morphology and ordered supramolecular structure. As for its ODS application, despite non-porous property of the catalyst, the surface catalysis could achieve excellent catalytic performance in multi-phase reactions by reaching complete conversion of dibenzothiophene in short time. Significant reaction factors upon the ODS process were investigated in detail. The repeated experiments verified its excellent stability in regular structure, chemical composition as well as catalytic performance. In the end, the mechanism of H_2O_2 activation by this catalyst was revealed with the assistant of Raman analysis.

1. Introduction

Nowadays, SO_x produced by combustion of sulfur-contained fuels in transportation and industry is one the main causes of air pollution. Considerable attentions have been attracted around the world on the deep desulfurization of fuels [1]. The conventional hydrodesulfurization (HDS) process is widely employed to reduce the sulfur content. However, HDS achieves limited performances in the removal of refractory sulfides, such as dibenzothiophene and its derivatives [2]. So far, alternative desulfurization technologies based on oxidation, extraction, adsorption etc. have been extensively investigated [3–5]. Among these attempts, oxidative desulfurization (ODS) is suggested as one of the most effective methods for its efficient removal of refractory sulfur compounds in mild conditions [6–9].

In a typical ODS process, S-compounds can be converted into their corresponding sulfones, followed by extractive or adsorptive removal of sulfones from the oxidized fuels to achieve deep desulfurization [10,11]. H_2O_2 is generally used as an oxidizing agent due to its high percentage of active oxygen, high reactivity and environmental benign properties [12–14]. Polyoxometalates (POMs), a class of structurally well-defined anionic metal-oxide clusters, have been widely employed as catalysts for oxidation owing to their notable redox feature [15]. The

interaction between POMs and H_2O_2 can produce active per-POM complexes for the efficient oxidation of refractory thiophenic compounds [16,17]. However, the use of heterogeneous catalysts in ODS process with H_2O_2 aqueous solution as oxidant brings about a liquid-liquid-solid three-phase reaction system [18]. Consequently, increasing the compatibility of catalysts with oily fuels is one of the effective methods to enhance the activity due to the inherent hydrophility of POMs clusters [19].

Recently, phase-transfer catalysts (PTC) which are developed by introducing phase transfer cationic groups to POMs were explored in ODS and led to good results [10,20–22]. The surfactant-type organic cations commonly with long carbon chain could improve the affinity to oil phase and capture the weakly polar sulfide molecules by hydrophobic-hydrophobic interactions [23]. However, as molecular catalysts, the POMs-based PTC bear bad separability in the reaction systems. Normally, the immobilization of PTC into porous materials can avoid its direct loss, but not always improved the activity due to the reducing of accessibility of catalytic sites in holes, especially in a multi-phase reaction system. Furthermore, the grafting procedure of PTC is complex. So, the development of amphiphilic catalysts with monolithic structure is still a challenge.

It is notable that POM clusters possess precise chemical

composition, uniform morphologies and delocalized multiple negative charges, which make them quite suitable for ionic self-assembly [24]. Some amphiphilic POM catalysts show interesting self-assembly behavior with the help of a solvent system [25–27]. More recently, the ionic self-assembly of POMs with multi-charged cations was proposed which enable adaptive encapsulation from small molecules to nanoscale materials [24]. Their potential applications range from catalysis and separation to responsive materials [28–31]. Multivalent electrostatic interactions between multi-charged cations and POMs play a fundamental role in creating unique and stable nanostructures [24]. Because the negative charges of the POMs are moveable within the cluster [32], cationic groups can spontaneously adjust their locations around the POMs depending on steric effect or multiple interactions. Based on the rational design, the construction of ionic organic–inorganic hybrids can be expected in principle.

In this work, novel POMs-based organic-inorganic hybrided nanowires were fabricated based on the ionic self-assembly principle. The preparation needs neither template agents nor toxic organic solvents, which is facile and environmentally friendly. Herein, *N,N'*-(1,4-phenylenebis(methylene))bis(*N,N*-dimethyldodecan-1-ammonium chloride) (Dda-pX-2Cl), an ionic compound with centrosymmetric organic bivalent cations, was synthesized and assembled with $Mo_8O_{26}^{4-}$ isopolyanions into anisotropy nanowires. Detailed assessments about their structure and construction characteristics were carried out by different techniques. The catalytic performance of the nanowire catalysts were tested by the ODS of model diesel with H_2O_2 aqueous solution (30 wt%) as an oxidant. Significant factors including reaction temperature, molar ratio of H_2O_2/S, catalyst dosage and sulfur species upon the ODS process were investigated in detail. The repeatability of the catalyst was also evaluated. Furthermore, the catalytic mechanism was proposed based on the Raman analysis.

2. Experimental section

2.1. Materials

1,4-Bis(chloromethyl)benzene (> 98%) and *N,N*-dimethyl dodecylamine (> 97%) were purchased form Tianjin Heowns Biochem LLC. Ethanol (> 99%), ethyl acetate (> 99%), n-octane (> 99%) and hydrogen peroxide (≥ 30 wt%) were purchased from Tianjin Jiangtian Chemical Technology Co., Ltd. Thiophene (T, > 99%), benzothiophene (BT, > 97%), dibenzothiophene (DBT, > 98%), 4,6-dimethyl-dibenzothiophene (4,6-DMDBT, > 97%) and ammonium heptamolybdate tetrahydrate ((NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O, 99.9%) were purchased from Aladdin Reagent Co. Ltd.

2.2. Synthesis of Dda-pX-2Cl

N,N-Dimethyl dodecylamine (0.1 mol) and ethanol (30 mL) were charged into a flask and vigorously stirred at 25 °C. Then, 1,4-bis (chloromethyl)benzene which dissolved in another 30 mL of ethanol was slowly added into the flask by use of a dropping funnel. The mixture was stirred at 25 °C for 2 h after dropping and further reacted at 50 °C for 48 h. After the reaction, the solvent was removed using rotary evaporation. The obtained solid product was dispersed in 50 mL ethyl acetate to remove to residual reactant, then filtered, washed with ethyl acetate for three time and dried under vacuum. ^{1}H NMR (VARIAN INOVA 500 MHz spectrometer) spectrum of Dda-pX-2Cl is shown in Fig. S1. Deducing from the ^{1}H NMR spectrum, the purity of Dda-pX-2Cl was not lower that 99%.

Dda-pX-2Cl: ^{1}H NMR (500 MHz, D$_2$O) δ 7.68 (d, *J* = 2.6 Hz, 4H), 4.62 (s, 4H), 3.21–3.06 (m, 16H), 1.85 (s, 4H), 1.41–1.10 (m, 36H), 0.85 (d, *J* = 6.9 Hz, 6H).

2.3. Preparation of the POM hybrid nanowires

The POM-based nanowires were prepared through a direct precipitation method. In short, Dda-pX-2Cl (2.00 mmol) was dissolved into 150 mL deionized water to form a solution A, and (NH$_4$)$_6$Mo$_7$O$_{24}$·4H$_2$O (1.15 mmol) was dissolved into 100 mL deionized water to form a solution B. The anion exchange reaction was done by slowly dropping the solution B into solution A by use of a syringe under magnetic stirring at 40 °C. The dropping rate was about 1 mL/min. Then, the mixture was moved into a hydrothermal reaction vessel and heated at 100 °C for 24 h. The white precipitates were then separated and washed with deionized water (50 mL, three times) successively by centrifugalization. The obtained solids were dried under vacuum at 80 °C for 24 h.

2.4. Characterization methods +

The Fourier transform infrared spectroscopy (FT-IR) of samples was recorded on a Bio-Rad FTS 6000 FT-IR spectrometer. Thermograms were recorded using the TGA instrument (Mettler Toledo TGA-DSC 1) with a weighing precision of ± 0.1% at a heating rate of 10 °C/min in the temperature range between 50 and 600 °C under an air atmosphere. CHN elemental analysis results were recorded on an Elemental analyser (Elementar Vario EL III). The surface morphologies of the catalysts were characterized by field emission scanning electron microscopy (SEM, Hitachi S-4800). Catalyst sample, H$_2$O$_2$ aqueous solution and their reaction system were characterized by a Raman Microscope and Spectrometer (Renishaw, inVia Reflex) with the excitation laser at 785 nm. Transmission electron micrographs (TEM) were taken with a Transmission Electron Microscope (JEOL JEM-2100F). The powder X-ray diffraction (XRD) analysis was carried out on a Bruker D8 diffractometer with high-intensity Cu Kα radiation (λ = 1.54 Å). X-ray photoelectron spectroscopy (XPS) data were obtained with an electron spectrometer (ULVAC-PHI, PHI 5000 VersaProbe). The leaching of Mo element in liquid phase was determined on a GBC-932 atomic adsorption spectrometer (AAS, GBC, made in Australia).

2.5. Desulfurization and analysis

Model oil was prepared by dissolving DBT in n-octane to reach 1000 ppm S-content. Model oils of T, BT, DBT and 4,6-DMDBT with S-content of 500 ppm were also prepared.

The ODS process was conducted in a 50 mL jacked reactor equipped with a circulator bath, a magnetic stirrer and a reflux tube. 10 g of model oil and certain amount of catalysts (20–50 mg) were added into the reaction, and stirred at 400 r/min. Then, H$_2$O$_2$ aqueous solution (30 wt.%), whose dosage was determined by H$_2$O$_2$/S proportion (2/1–6/1), was charged into the reactor to start the reaction. Samples were taken from the oil phase at set intervals and analyzed by GC-FID (Agilent 7890A; HP-5, FID: Agilent) for the evolution of S-compounds concentration.

The conversion rate of the sulfides was calculated as follows:

$$S_{conversion} = \frac{C_0 - C_t}{C_0} \times 100\%$$

where C_0 is the initial concertration of model sulfide in the model oil and C_t is its concentration in the oil phase after the reaction began for a certain amount of time. GC information is summarized in Table S1, and the GC-FID profiles of the model oil before and during the reaction are shown in Fig. S2.

3. Results and discussion

3.1. Formation and characterization of hybrid nanowire

The POMs-based hybrid was prepared according to the route shown in Scheme 1. Dda-pX-2Cl, an ionic compound, has a linear