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Mono Mn(II)-substituted phosphotungstate@modified graphene oxide as a high-performance nanocatalyst for oxidative demercaptanization of gasoline

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ABSTRACT

In this study, the removal of hazardous sulfur compounds from gasoline was provided based on catalytic oxidation demercaptanization technique. The cesium salt of mono Mn(II)-substituted Keggin-type polyoxometalate $Cs_5PMnW_{11}O_{39}$ ($PMnW_{11}$) was successfully synthesized and immobilized on modified graphene oxide (mGO) as a new nanocatalyst ($PMnW_{11}$@mGO) for demercaptanization process. The synthesized materials were characterized by powder X-ray diffraction (XRD), scanning electron microscopy (SEM), ultraviolet–visible (UV–vis), Fourier transform infrared spectroscopy (FT-IR), and cyclic voltammetry (CV) analysis. Characterization of the prepared nanocomposite was confirmed that the structures of the $PMnW_{11}$ and mGO were retained after immobilization. The sulfur-containing molecules in real gasoline and simulated fuel were oxidized and extracted efficiently under mild reaction condition. After treatment, the mercaptans and total sulfur content of real gasoline were lowered with 98.8% and 98% yield, respectively. The $PMnW_{11}$@mGO hybrid nanocatalyst was separated and reused conveniently at the end of the reaction for five times. The excellent performance of this new catalytic oxidation system can be a promising rout to achieve ultra-clean gasoline.

Introduction

Combustion of transportation fuels containing high concentrations of sulfur compounds is the main sources of air pollution [1]. Among the various kinds of low-molecular-weight sulfur compounds in gasoline such as hydrogen sulfides (H_2S), alkyl mercaptans (RSH), carbon disulfides (CS_2), and thiophenes, mercaptans have disagreeable odors. Furthermore, these volatile organic compounds have adverse effects on transport lines and storage sites due to their acidity, toxic, and corrosive properties [2–4]. Therefore, decreasing the sulfur and mercaptans level in the petroleum products is the most important aspect for petroleum refineries and environmental protection. In this regard, the catalytic oxidation desulfurization and demercaptanization have been developed as efficient and affordable strategy for removal of various sulfur compounds under mild conditions [4,5]. According to these approaches, sulfur-containing molecules are selectivity oxidized into their corresponding sulfones and disulfides by using an oxidizing reagent in the presence of appropriate catalysts [6–8]. Polyoxometalates (POMs) are a unique class of negatively charged metal-oxygen clusters with a wide structural variety and interesting properties. [9,10]. Because of their unique features such as high thermal stability, high oxidation potential, and fast reversible multi-electron redox transformations, POMs are effective catalysts in homogeneous and heterogeneous systems [11–13]. Keggin-type polyoxoanions with abundant terminal oxygen atoms are a subclass of this family that have been found to be highly active catalysts in oxidation reactions [14,15]. Nevertheless, the two main limitations of POMs are low specific surface areas and high solubility in aqueous media, which make them difficult to separate and reuse [16]. For overcoming these drawbacks, the synthesis of POM-supported catalysts has gained increasing attention in recent years. Also, there has been growing interest in using mGO as a various materials carrier for improving the catalytic performance of catalysts in heterogeneous reactions due to its chemical stability, electronic conductivity and high specific surface area [17–20]. As a part of our ongoing efforts for developing the synthesis and application of POMs [21–24], herein we report

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the preparation of $PMnW_{11}$@mGO as a high-performance nanocatalyst for the elimination of organic sulfur compounds. To the best of our knowledge, this is the first reported results of the application of this catalyst for demercaptanization of gasoline. The hybrid nanocomposite is successfully prepared by reaction of mGO and $PMnW_{11}$ under stirring for 24 h. In typical oxidation reactions, the mixture of H_2O_2/CH_3COOH is used as oxidant and polar CH_3CN applied as an extraction solvent for removing the oxidized products. In addition, the influences of different parameters on the demercaptanization efficiency are investigated in detail.

Experimental

Materials and characterization methods

Phosphoric acid (98 wt.%), sulfuric acid (98 wt.%), graphite powder, phosphotungstic acid hydrate ($H_3PW_{12}O_{40}.nH_2O$), hydrochloric acid (37 wt.%), and diethyl ether (99%) were purchased from Merck chemical company. H_2O_2 (30%), ethanol (96%) were supplied by Fluka. Other reagents were of analytical grade from Merck and were used as received. The sulfur compounds for the preparation of simulated fuel and chemicals, including 4-methyl thiophenol, *n*-butyl mercaptan, 4-chloro thiophenol, and solvent (*n*-heptane) were obtained from Aldrich Company. Typical real gasoline (density 0.7977 g mL^{-1} at 15 °C, total sulfur content 0.497 wt.%) was used. Powder X-ray diffraction (XRD) patterns were carried out on a D8 Bruker Advanced, X-ray diffractometer using Cu Kα radiation (α = 1.54 Å) with continuous scan mode. FT-IR spectra were taken with a Matson FT-IR spectrophotometry with KBr disks in the range of 400–4000 cm^{-1}. UV–vis spectra were recorded with a Shimadzu 160 spectrophotometer. Moreover, the cyclic voltammetry (CV) measurements were performed with a Biologic potentiostat/galvanic with a three-electrode cell configuration using Pt wire, Ag/AgCl saturated electrode, and glassy carbon (3 mm, ϕ) as counter, reference, and working electrodes, respectively, in H_2SO_4 (1 M). The electrode ink was prepared by dispersing 5 mg of a sample in 125 μL of isopropyl alcohol and 125 μL of deionized (DI) water, was added finally. The glassy carbon (GCE) working electrode was polished in a diamond solution and a 0.05 μm Al_2O_3 paste before coating ink on the surface of the GCE. Then, 3 μL of well-dispersed ink was dropped onto the glassy carbon surface and dried at room temperature in order to form a uniform thin film of the catalyst. All CV measurements were recorded using a potential window between −0.2 and 0.8 V at different scan rates. A nitrite oxidation reaction was carried out using different concentrations from 100 μM to 600 μM $NaNO_2$ at a 10 mV s^{-1} scan rate. A long-term electrochemical stability test was performed up to 100 cycles at a 50 mV s^{-1} scan rate under the same conditions. The total sulfur and mercaptan content in real gasoline before and after the reaction were determined using X-ray fluorescence ASTM D-4294 and D-3227 standard test methods. These standard test methods provide the precise and rapid measurement of total sulfur in petroleum and petroleum products with a minimum of sample preparation. A typical analysis time is 1–5 min per sample.

Synthesis of catalyst

Synthesis of graphene oxide (GO)

A graphene oxide (GO) was synthesized from graphite powder using Hummer's method [25]. Briefly, 360 mL of concentrated H_2SO_4 was mixed with 40 mL of H_3PO_4. Then, this solution was added to a flask containing 3.00 g graphite and 18.00 g $KMnO_4$, and heated up to 35–40 °C. The reaction was then heated to 50 °C and stirred for 12 h. The resulting solution was allowed to cool down to room temperature and poured into 400 mL ice bath with 3 mL of H_2O_2 (30%). Next, the mixture was sprinkled by using a metal U.S. Standard testing sieve (W.S. Tyler, 300-m) and then filtered by polyester fiber (Carpenter Co.). After that, the filtrated solution was centrifuged (4000 rpm for 4 h), and decanted away. The residual solid material was washed with 200 mL of DI water, 200 mL of ethanol, and 200 mL of 30% HCl several times. Finally the resulting material was coagulated through 200 mL of ether, and the residual suspension was filtered over a polytetrafluoroethylene (PTFE) membrane with a 0.45 nm pore size. The obtained precipitate was vacuum-dried overnight at room temperature.

Synthesis of reduced graphene oxide (rGO)

In a typical reaction, 1.00 g of the synthesized GO was dispersed in 250 mL of DI water. Afterward, 5 mL of hydrazine hydrate was added to the above mixture and continued stirring for 4 h at 100 °C under a nitrogen atmosphere. Ultimately, the resulting solution was filtered and washed until the neutral pH was reached, and then dried for 24 h at 40 °C in a vacuum oven.

Synthesis of modified graphene oxide (mGO)

The mGO was prepared as follows: 0.10 g of prepared rGO was dispersed in 50 mL of toluene for 30 min. Next, 0.10 g of 3-aminopropyl-triethoxysilane (APTES) was added to the rGO dispersion solution. The resulting solution was stirred in the condensation reaction at 30 °C for 3 h and at 100 °C for 3 h under nitrogen atmosphere. For removal of the residual APTES, the final solution was washed with toluene, filtered, and dried for 24 h in the oven at 40 °C.

Synthesis of cesium salt of mono Mn(II)-substituted phosphotungstate ($Cs_5[PMnW_{11}O_{39}]$)

The $Cs_5[PMnW_{11}O_{39}]$ was synthesized as follows: 2.88 g of $H_3PW_{12}O_{40}\cdot nH_2O$ was dissolved in 10 mL of DI water and the pH of the solution was adjusted to 4.8 using NaOH (1 M). This solution was heated at 90 °C with stirring for l h. Subsequently, a solution of 0.20 g of $MnCl_2$ in 10 mL of DI water was added to the stirred solution and 10 mL of concentrated CsCl was added slowly. Then, the remained orange solid product $Cs_5[PMnW_{11}O_{39}]$ (designated as $PMnW_{11}$) was cooled down to room temperature, washed with ether and dried for 24 h at 40 °C.

Synthesis *of the $PMnW_{11}$@mGO nanocatalyst*

The $PMnW_{11}$@mGO nanocatalyst was synthesized according to Scheme 1. Firstly, the prepared mGO (0.1 g) was dispersed in 20 mL DI water and sonicated for 30 min by using an ultrasonic bath (Bandelin Sonorex Digitec). Then, aqueous solution of 0.02 g mL^{-1} of $PMnW_{11}$ was added and stirred for 24 h. Finally, the resulting precipitate was washed and filtered for three times with DI water to remove the residual adsorbed materials and was allowed to dry at 60 °C overnight in a vacuum oven.

Catalytic tests

Demercaptanization of simulated fuel

In a typical run, the demercaptanization process was carried out in a round-bottom flask equipped with a magnetic stirrer and a thermometer. Some of the mercaptan sulfur compounds (MerSCs) such as 4-methyl thiophenol, 4-chloro thiophenol, and *n*-butyl mercaptan were dissolved in *n*-heptane as a simulated fuel to evaluate the catalytic performance of $PMnW_{11}$@mGO and the reactivity of MerSCs in the oxidation reaction. The water bath was heated up and the reaction temperature was maintained at 25–40 °C. The prepared fuel containing 200 ppm of sulfur content was mixed with 3 mL of H_2O_2/CH_3COOH in the volume ratio of 2/1 to in-situ formation of CH_3COOOH as an oxidant. Following this condition, 0.1 g of nanocatalyst ($PMnW_{11}$@mGO) was added to the