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Synthesis and characterization of new nanocomposite CTAB-PTA@CS as an efficient heterogeneous catalyst for oxidative desulphurization of gasoline

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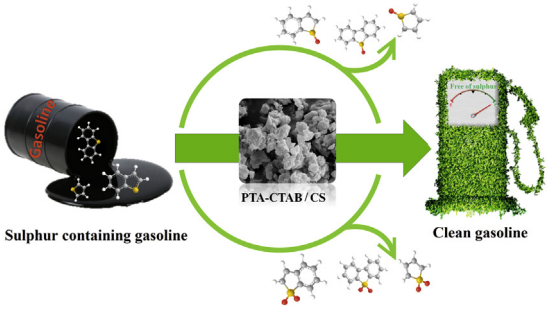
HIGHLIGHTS

- The catalyst PTA-CTAB@CS was synthesized under sonication condition.
- The catalytic activity of nanocomposite was tested on the ODS of gasoline.
- PTA-CTAB@CS was shown be able to remove S-compounds (with high yield) in gasoline.
- The nanocatalyst could be separated and recycled easily after five runs.

GRAPHICAL ABSTRACT



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ABSTRACT

In order to obtain the clean gasoline fuel, a new nanocomposite, CTAB-PTA@CS has been introduced as an efficient and green catalyst for oxidative desulphurization (ODS) process. The nanocomposite was successfully prepared by reaction of cetyltrimethylammonium bromide (CTAB), phosphotungstic acid (PTA), and chitosan (CS) at room temperature under sonication condition. The organic-inorganic hybrid characterized by FT-IR, UV–vis, XRD, and SEM techniques. The catalytic activity of nanocomposite was tested on real gasoline fuel in the presence of CH_3COOH/H_2O_2 in the volume ratio of 1/2 as oxidant system. Additionally, the results are compared with that oxidation process of prepared model sulphur compounds (MSCs) at the same conditions. After one hour, the results were shown that the removal of mercaptans and total sulphur content could be reduced to 98% and 95% at the temperature of 35 °C. The main factors affecting the desulphurization efficiency, including catalyst dosage and temperature were investigated in detail. In addition, the kinetic parameters of oxidation of MSCs, reaction mechanism, and reusability of catalyst were discussed. This system provides an environmentally friendly, feasible and new catalytic method for the production of low-sulphur gasoline fuel.

1. Introduction

The organic sulphur-containing compounds in transportation fuels can produce toxic sulphur oxide gasses by the combustion, which have caused adverse effects on the environment [1]. Mercaptans as a kind of sulphur compounds are undesirable because of their foul odors and corrosive properties [2]. Therefore, desulphurization of fuels is extremely important to environmental safety that has become a main challenge of the world. To achieve this purpose, global sulphur levels to be limited to less than 15 ppm in the near future [3]. The conventional hydrodesulphurization (HDS) method shows high efficiency in elimination of thiols, sulfides, and mercaptans in gasoline and diesel at industrial

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scale [4]. However, it is less effective in treating refractory alkylated organic sulphur compounds like dibenzothiophene and its derivatives caused by the steric hindrance of these compounds [5,6]. Mentioned technology requires too high temperatures, high pressures, and high hydrogen consumption. Therefore, HDS is not suitable for affordable reduction of the sulphur content from fuel [7,8]. Among the developed desulphurization approaches, including bio desulphurization [9], extractive desulphurization [10], adsorptive desulphurization [11], oxidative desulphurization can be oxidized the alkylated sulphur compounds to sulfoxides and sulfones under moderate reaction conditions (at below 100 °C and ambient pressure) without expensive hydrogen consumption [12]. Then, these oxidized products which have the higher polarity than sulphur can be removed directly by a water-soluble polar solvent like acetonitrile (CH_3CN) [13]. In ODS system, a high oxidant-to-sulphur ratio is required to oxidize sulphur compounds. But, this problem can be improved by using of suitable catalysts. Heteropolyoxometalates (HPOMs) as a catalyst were shown excellent catalytic activities for the oxidation sulphur-containing compounds because of their unique properties, including high thermal stability, super acidity and tunable redox potential [14–17]. However, the catalytic performance and reusability of the bulk HPOMs are limited due to their low specific surface areas and high solubility in aqueous solution [18,19]. These drawbacks can be avoided by using different methods such as dispersing HPOMs on solid supports with high surface areas and immobilizing them into an organic polymer to form heterogeneous recyclable catalysts [20]. Chitosan is a natural polymer consisting of reactive hydroxyl and amino functional groups. The main application of this polysaccharide depends on the electrostatic interaction between cationic amino groups and anionic surface-active sides of substances, such as heteropolyanions. In addition, CS is biocompatibility, non-toxicity; expressed chelating polymer and the adsorption abilities of CS has been proved for organic contaminants and some toxic ions [21–23]. Therefore, CS is suitable candidates as matrices for assembling HPOMs to obtain an organic-inorganic nanocatalyst with higher surface areas than the bulk HPOMs with sulphur removal properties. In continuation of our previous investigation on the synthesis and application of polyoxometalates [24–27], and as a part of our ongoing research program to develop ODS of gasoline, we hereby report for the first time, synthesis of new nanocomposite as a new nanocatalyst for ODS of gasoline. In the presence of CTAB with long alkyl chain as a countercation, PTA was immobilized on CS in acidic media at room temperature under sonication condition. Countercation with quaternary ammonium salts with lipophilic cation can act as phase transfer agent and transfer the peroxometal anion into organic phase [27]. The green nanocatalyst (CTAB-PTA@CS) was synthesized and used as an efficient catalyst for selective ODS of prepared MSCs and real gasoline with CH_3COOH/H_2O_2 as an oxidant. After the oxidation step, the polar extracting solvent (CH_3CN) was used for extraction of oxidized sulphur compounds. The catalyst was separated and reused at the end of the reaction. The chemical characterization of this nanocomposite was accomplished by XRD, FT-IR, SEM, and UV–vis analyses.

2. Experimental

2.1. Materials

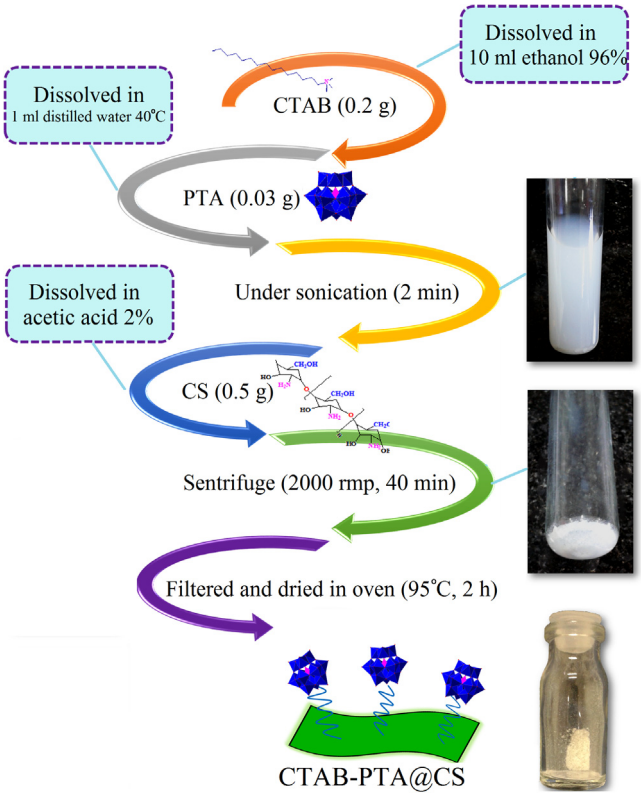
All solvents and reagents which are used in synthesized procedure are available commercially and were used as received, without any further purification. A model containing sulphur compounds and chemicals, including thiophene (Th), benzothiophene (BT), dibenzothiophene (DBT) and solvent (n-heptane) for experiments, hydrogen peroxide (30 vol.%), CS (low molecular weight with a degree of deacetylation of 75–85%), CTAB, PTA, acetic acid and ethanol (96%) were purchased from Sigma–Aldrich company. Typical real gasoline (density 0.7868 g/mL at 15 °C, total sulphur content 0.428 wt.%) was used.

2.2. Preparation of nanocatalyst

The CTAB-PTA@CS nanocatalyst was synthesized according to Scheme 1. A solution of CTAB (0.2 g, 0.55 mmol) in 10 mL ethanol (96%) was added to a solution of the PTA (0.03 g, 0.01 mmol) in 1 mL distilled water at room temperature. Then 0.5 g of CS was dissolved in a solution of 2% acetic acid to obtain a clear solution. The mixture of PTA and CTAB was added drop-wise to CS solution under sonication in ultrasonic water baths (frequency 35 kHz mains connection 230 V) for 2 min. The milky white suspension is precipitated by centrifugation (2000 rpm, 40 min). Finally, the obtained white precipitate was filtered and dried in an oven at 95 °C for 1.5 h.

2.3. Characterization of nanocatalyst

The Fourier Transform Infrared spectroscopy (FT-IR) studies were done on a Thermo-Nicolet-is 10 spectrometer, using KBr pellets technique with a measuring range 400–4000 cm^{-1}. Ultraviolet–visible (UV–vis) spectra were recorded with a double beam Thermo-Heylos spectrometer in the range of 200–500 nm. Measurements were performed by using quartz cuvettes. Powder X-ray Diffraction (XRD) analysis was carried out on a Bruker D8 advance powder X-ray diffractometer with a Cu-Kα (λ = 0.154 nm) radiation source, and the data were collected from 10° to 80° (2θ). The surface morphologies were characterized with Scanning Electron Microscope (SEM) by LEO 1455 VP with an accelerating voltage of



Scheme 1. Schematic description of the procedure to prepare CTAB-PTA@CS.