



## ORIGINAL ARTICLE

# Oxidative desulfurization of diesel by potato based-carbon as green support for $H_5PMo_{10}V_2O_{40}$ : Efficient composite nanorod catalyst



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Received 7 November 2016; revised 22 February 2017; accepted 23 February 2017

Available online 7 March 2017

## KEYWORDS

Green catalyst;  
Nanorod catalyst;  
Potato;  
Oxidative desulfurization;  
Diesel

**Abstract** The C@POM (carbon@polyoxometalate) containing  $H_3PMo_{12}O_{40}$  ( $PMo_{12}$ ),  $H_5PMo_{10}V_2O_{40}$  ( $PMo_{10}V_2$ ),  $H_6PMo_9V_3O_{40}$  ( $PMo_9V_3$ ),  $H_7PMo_8V_4O_{40}$  ( $PMo_8V_4$ ),  $H_3PW_{12}O_{40}$  (PW), and  $H_4SiW_{12}O_{40}$  (SiW) were prepared from natural potato as green, and cheap catalyst support source. The C@ $PMo_{10}V_2$  was found to be a unique, effective, and eco-friendly catalyst for selective oxidation of sulfides, using 30% aq.  $H_2O_2$ . C@ $PMo_{10}V_2$  composite was characterized by X-ray diffraction spectroscopy (XRD), energy dispersive X-ray spectroscopy (EDX), scanning electron microscopy (SEM), thermal gravimetric analysis (TGA), Fourier transform infrared (FT-IR) spectrophotometry, zeta sizer, and zeta potential. The XRD results show that during immobilization  $PMo_{10}V_2$  on the carbon catalyst support (CCS), the crystallite structure of  $PMo_{10}V_2$  and CCS was not changed. The SEM results show that  $PMo_{10}V_2$  crystals deposited on the surface CCS rods as composite nanorod structure. A variety of sulfides, sulfur-containing model and real oil were oxidized with the C@ $PMo_{10}V_2/H_2O_2$  at room temperature. Recovered catalyst show excellent activity for at least four repeating cycles.

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## 1. Introduction

Among all elements, carbon constructs the greatest varieties of compounds in the world. Carbon is a versatile element because it can form various structures [1] such as nanotubes, nanorods, nanospheres, nanoplates, nanogranules, nano-onions, glassy carbon, carbon aerogels, and pyrolytic carbon. Recently, agricultural byproducts and renewable plant resources have also become attractive precursors to prepare carbon materials [2–7]. However, carbon compounds prepared from natural precursors have not been studied as much as other carbon

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Peer review under responsibility of King Saud University.



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sources, but are expected to possess various advantages over other carbon compounds, and have many applications. Besides, low cost, sustainability, natural abundance, biodegradability, and biocompatibility of these materials are the major advantages that surmount serious environmental problems [8,9]. However, one dimensional carbon materials prepared from natural precursors have not been studied as much as spheres and granules, but are expected to possess various advantages over spheres and granules as catalyst support.

Green and sustainable chemistry can be defined as the designing of products or processes that minimize the use and generation of hazardous substances [10,11]. To implement this goal, introduction of green, efficient, and selective catalytic system for desulfurization of sulfur content of diesel toward sulfoxides or sulfones has been receiving considerable interest in recent decades. Interestingly the production of light oil, with very low level of sulfur, was investigated by scientists. Sulfoxides and sulfones as polar molecules were easily extracted from real diesel by appropriate methods. Very recently, more and more groups have turned their attentions to polyoxometalates (POMs) and POM-based catalysts as efficient active species for hydrogen peroxide-based oxidation of sulfides, such as Fe@Si-PMo<sub>12-n</sub>V<sub>n</sub> [12], PPh<sub>4</sub>[MO(O<sub>2</sub>)<sub>2</sub>L] (M = Mo or W) [13], WO<sub>3</sub>/MCM-48 [14], Na<sub>2</sub>WO<sub>4</sub>/C<sub>6</sub>H<sub>5</sub>PO<sub>3</sub>H<sub>2</sub>/[CH<sub>3</sub>(n-C<sub>8</sub>H<sub>17</sub>)<sub>3</sub>N]HSO<sub>4</sub> [15], WO<sub>4</sub><sup>2-</sup>/silica-NH<sup>3+</sup> [16], PMo@HKUST-1 [17,18], ILs [19], and PW-ILs [20]. In oxidation process, H<sub>2</sub>O<sub>2</sub> has been widely used as the oxidant for the reason that it is cheap, commercially available, nontoxic, non-polluting and less corrosive than other oxidants [21,22].

The POMs in the bulk form possess very low surface area and high solubility in polar medium, which limits the exertion of potentially catalytic performance and makes some difficulties in catalyst recovery [23]. Many efficient supports were developed for preparing nanoscale POM particles at heterogeneous systems [24–26]. Using environmentally friendly heterogeneous catalysts based on natural ingredients is of interest and remarkable to many researchers.

Selective oxidation of sulfides to sulfoxides or sulfones requires highly selective catalyst. Therefore, we synthesized POMs including H<sub>3</sub>PMo<sub>12</sub>O<sub>40</sub> (PMo<sub>12</sub>), H<sub>5</sub>PMo<sub>10</sub>V<sub>2</sub>O<sub>40</sub> (PMo<sub>10</sub>V<sub>2</sub>), H<sub>6</sub>PMo<sub>9</sub>V<sub>3</sub>O<sub>40</sub> (PMo<sub>9</sub>V<sub>3</sub>), H<sub>7</sub>PMo<sub>8</sub>V<sub>4</sub>O<sub>40</sub> (PMo<sub>8</sub>V<sub>4</sub>), H<sub>3</sub>PW<sub>12</sub>O<sub>40</sub> (PW), and H<sub>4</sub>SiW<sub>12</sub>O<sub>40</sub> (SiW) coated carbon (C@POM) from natural abundant potato as the carbon catalyst support (CCS) *via* hydrothermal treatment at aqueous solvent as a green synthetic method. Catalytic activities of these catalysts were investigated in selective oxidation of sulfides. Desulfurization of model and real oil were also investigated under these reaction conditions.

## 2. Experimental

### 2.1. Materials and methods

The natural potato extraction of agronomy grounds in IRAN. Analytical grades of PMo<sub>12</sub>, PMo<sub>10</sub>V<sub>2</sub>, PMo<sub>9</sub>V<sub>3</sub>, PMo<sub>8</sub>V<sub>4</sub>, PW, SiW, solvents, sulfides, and hydrogen peroxide (30% aq. H<sub>2</sub>O<sub>2</sub>) were purchased from Merck and were used without further purification. The light cycle oil (LCO) feed was supplied from a refinery in Iran. X-ray diffraction (XRD) patterns were recorded by an Inel French, EQUINOX 3000 model X-ray diffractometer using Cu K $\alpha$  radiation. Scanning electron

microscopy (SEM) has been performed using an AIS2300C microscope with scanning range from 0 to 20 keV. Energy dispersive X-ray (EDX) measurements were made with an IXRF model 550i attached to SEM. Wavelength dispersive X-ray (WDX) spectroscopy has been performed by AIS2100 microscope model. SEM/EDX/WDX samples were prepared by coating of solid particles into a conductive layer. Thermogravimetric analysis (TGA) was carried out using a thermal gravimetric analysis instrument (Shimadzu TA-60WS-TGA-50/50H) with a flow rate of 30 mL min<sup>-1</sup> and a heating rate of 10 °C min<sup>-1</sup> in N<sub>2</sub>. The Fourier transform infrared spectrophotometry (FT-IR) of the samples were recorded at room temperature using a Bruker, ALPHA spectrophotometer at a spectral resolution of 4 cm<sup>-1</sup> using KBr pellets in the range of 400–4000 cm<sup>-1</sup> with a delicate beam condenser and a liquid nitrogen cooled MCT-Detector. The size distribution and surface charge of the samples were obtained using a laser particle size and zeta potential analyzer (HPPS5001, Malvern, UK). Total sulfur (TS) contents were determined using an Analytic Jena AG-multi EA® 3100 Element Analyzer. Thin layer chromatography (TLC) on pre-coated silica gel Fluorescent 254 nm (0.2 mm) on aluminum plates was used for monitoring progress of the reactions.

### 2.2. Preparation of CCS

The CCS was prepared as follows: in a typical method, at first the natural potato was manually peeled and stored in vacuum oven at 30 °C. Then 5 g of the stabilized sample was dispersed in distilled water (50 ml) under magnetic stirring. The homogeneous solution was transferred to a 100 ml Teflon-line stainless steel autoclave. The autoclave was sealed and maintained at 180 °C for 12 h in a digital temperature-controlled oven. After thermal treatment, the autoclave was cooled to room temperature and the resulting black precipitate was collected and centrifuged with distilled water for several times and finally dried in vacuum oven at 50 °C.

### 2.3. Preparation of the catalyst

For the immobilization of 40 wt.% of POM on CCS, 0.3 g of POM was dissolved in 1 mL of distilled water. This solution was added dropwise to a suspension of 0.5 g CCS in distilled water (50 mL) under sonication. The mixture was stirred at room temperature overnight. Finally, the solvent was removed using rotary evaporator and dried. After preparation, the catalyst calcined for 2 h at 150 °C. Preparation conditions for all catalysts were equalized. The yield was more than 90% for all catalysts.

### 2.4. General procedure for the oxidation of sulfides

#### 2.4.1. Oxidation of sulfides to sulfoxides and sulfones

A suspension of the sulfide (1.0 mmol), and catalyst (0.01 g) in EtOH:n-heptane (1:1 v/v, 3 mL), 30% aq. H<sub>2</sub>O<sub>2</sub> (3.0 mmol) was added. The resulting mixture was mixed at room temperature for appropriate time under aerobic conditions. Progress of the reaction was monitored by TLC. After completion of the reaction, the catalyst was removed by a repeated centrifugation (2000 rpm, 3 min) and decanted. Catalyst was collected and treated with 1,2-dichloroethane (DCE) for

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