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An organic–inorganic hybrid compound constructed by polytungsto-vanadosilicate and hexadecyltrimethyl ammonium as an efficient catalyst for demercaptanization of crude oil

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ABSTRACT

$[C_{16}H_{33}N(CH_3)_3]_4H_3SiV_3W_9O_{40}$ has been synthesized by reaction of $Na_{10}[\alpha\text{-}SiW_9O_{34}]$ with sodium vanadate and encapsulated by cetyltrimethyl ammonium. Then this organic–inorganic hybrid compound condensation with titanium tetraisopropoxide at 100 °C via sol–gel method under oil-bath condition. $[C_{16}H_{33}N(CH_3)_3]_4H_3SiV_3W_9O_{40}\text{-}TiO_2$ was prepared. The materials characterized by IR, XRD, TEM and UV–vis techniques. This alkyl ammonium keggin- type nanoparticle be able to scavenge mercaptans and hydrogen sulfide (with high yield) in the presence of H_2O_2. This system provides a practical, convenient and efficient method for scavenging of sulfur compound in light and heavy crude oil.

Introduction

The environmental pollution of sulfur compounds produced by refineries is of great concern. There is a great need of producing cleaner fuels [1] and ultra-low-sulfur fuels used in fuel cell applications [2]. Mercaptans are a kind of organic sulfides and widely existing in petroleum products. Mercaptan sulfur has an objectionable odor, an adverse effect on fuel system elastomers, and is corrosive to fuel system components. They cause foul odors and deteriorate the finished products. In addition, due to their acidity, they are corrosive to metals, which is harmful for storage and usage of oil products [3–8]. Therefore, it is necessary to remove them, either by extracting or by transforming them to innocuous disulfides. Such processes are usually called sweetening in the petroleum industry. In continuation of our group research on the syntheses and application of polyoxometalates in organic reactions [9–16] and due to the importance of derivatives of disulfides in biological and chemical processes, we hereby report the applicability of POM-TiO_2 for efficient demercaptanization of light and heavy crude oil. General oxidation reaction of mercaptans that introduces disulfides as major part of mercaptans oxidation products is in common in all processes of catalytic oxidation of mercaptans:

$$2RSH + 1H_2O_2 \rightarrow 1RSSR + 2H_2O \quad (1)$$

We wish to report a very efficient, convenient and practical method for oxidative of mercaptans into the corresponding disulfides using hydrogen peroxide as an oxidizing reagent catalyzed by the $[C_{16}H_{33}N(CH_3)_3]_4H_3SiV_3W_9O_{40}\text{-}TiO_2$ nanocomposite under mild conditions.

The application of polyoxometalates (POMs) as catalytic materials is increasing continuously in the catalytic field. Because of their high thermal stability, stronger acidity, high hydrolytic stability (pH 0–12), safety, quantity of waste, reusability, corrosiveness, separability, high oxidation potential and greenness, in this context, polyoxometalates (POMs) are promising catalysts [9–15]. Supporting the heteropolyacids on solids with high surface areas improves their catalytic performance in various heterogeneous reactions [17–19]. Emulsion catalysts like $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ and $[C_{18}H_{37}N(CH_3)_3]_4[H_2NaPW_{10}O_{36}]$ have been found to reduce the sulfur contents of diesel oil from more than 500 μg/g to less than 30 μg/g under mild conditions, and they can be recycled with 100% selectivity [20,21]. Tetra butyl ammonium salts of $[V(VW_{11})O_{40}]^{4-}$were found to decrease the

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Table 1
Properties of crude oil.

Entry	Properties of crude oil	Method	Results
1	Specific gravity @ 60/60 °F	ASTM D1298	0.8442
2	Density @ 15 °C	ASTM D1298	0.8438
3	API GR. @ 60/60 °F	Calculated	36.11
4	Water content by distilation vol. %	ASTM D4006	0.025
5	Sediment by extraction vol. %	ASTM D473	0.01
6	Total sulfur content % wt	ASTM D4294	0.9842
7	Pour point (°C)	ASTM D97	−12
8	Mercaptans ppm	ASTM D3227	208.02
9	Total acidity mg KOH/gr	ASTM D664	0.12
10	Salt ptb	ASTM D3230	28

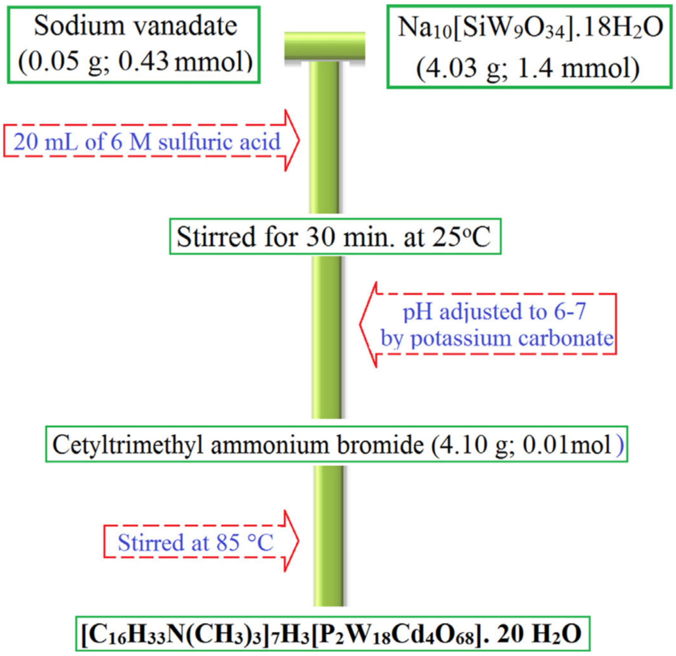
Abbreviation: API GR.; API gravity (API – American Petroleum Institute); API = 141.5/Specific gravity -131.5.

sulfur contents of gas oil by up to 90% in the presence of H_2O_2 [22]. A phase transfer between the aqueous phase containing the oxidants and catalyst and the organic phase containing the oil limits the overall efficiency. This aspect of the process can be improved by using a phase transfer agent that facilitates the transfer of reagents between the two immiscible phases. A new approach to phase transfer catalysis uses surfactant based or amphiphilic catalysts, which combine together a heteropolyoxometalate anion and a quaternarnary ammonium cation. Therefore we designed via sol–gel method under oil-bath condition, anatase TiO_2 crushed nano leaf coupled by quaternary ammonium mixed-addenda vanadium-containing keggin type polyoxometalate at 100 °C, as a phase transfer catalyst for oxidative of mercaptans in light and heavy crude oil. The chemical characterization of this compound was accomplished by means IR, XRD, TEM and UV–vis techniques.

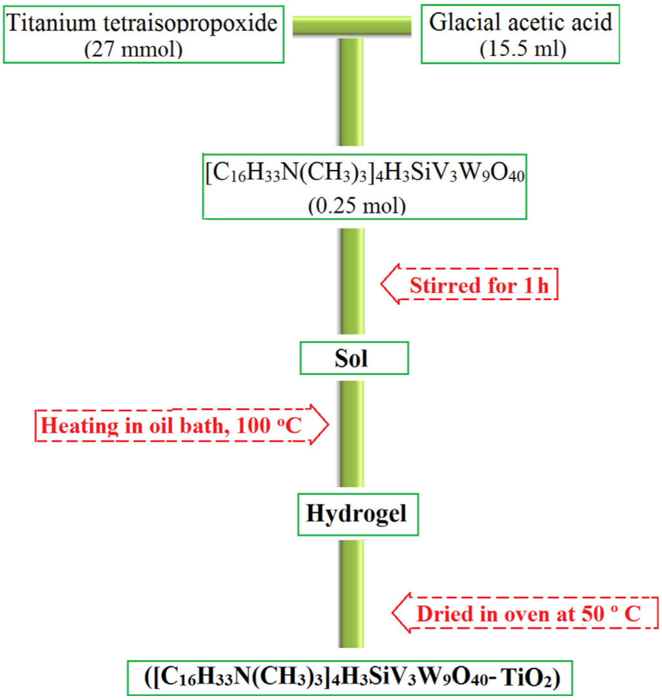
Experimental

Materials

All reagents and solvents used in this work are available commercially and were used as received, unless otherwise indicated. Previously reported methods were used to purify the mercaptans and thiols [12]. Preparation of mixed heteropolyacids and salts were based on a literature procedure with the following modifications [9,11]. Titanium (IV) tetraisopropoxide was obtained from Merck Chemical Company. All chemicals were purchased from Merck and used without purification. Hydrogen peroxide (30 vol.%) and solvent (n-heptane) for experiments and analysis and were obtained from Aldrich Chemical Company. Crude oil (density 0.8438 g/mL at 15 °C, Total mercaptan content 208 ppm) was supplied from the terminal of south Iranian Oil Company (Table 1).



Scheme 1. Chart of synthesis of catalyst.



Scheme 2. Chart of synthesis of nanocatalyst.

Preparation of mercaptan scavenger $[C_{16}H_{33}N(CH_3)_3]_4H_3SiV_3W_9O_{40}]$

The $[C_{16}H_{33}N(CH_3)_3]_{y-x}H_x[Si\ W_{12-x}V_xO_{40}]$. nH_2O ($x = 3, 2, 1$ and $y = 7, 6, 5$) was prepared as following: First, in 30 mL of distilled water, sodium vanadate (0.05 g; 0.43 mmol) is dissolved. To the stirred solution is added $Na_{10}[SiW_9O_{34}]$. $18H_2O$ (4.03 g; 1.4 mmol), followed by 20 mL of 6 M sulfuric acid. Then, for 30 min, the solution is maintained under stirring. By addition of solid potassium carbonate, the pH is adjusted between 6 and 7. By addition of solid potassium chloride (2.2 g) an orange potassium salt (2.5 g) is precipitated and recrystallized in water. The

Table 2
Demercaptanization of *n*-Butyl Mercaptan by CTA-SiPOM-TiO_2.[a]

Entry	Different demercaptanization system	*n*-Butyl Mercaptan conversion (%)	
		With H_2O_2	Without H_2O_2
1	$[C_{16}H_{33}N(CH_3)_3]Cl$	5.6	–
2	$Na_7SiV_3W_9O_{40}$	72	29.5
3	$H_7SiV_3W_9O_{40}$	86.3	35.2
4	$[C_{16}H_{33}N(CH_3)_3]_7SiV_3W_9O_{40}$	91.5	47.3
5	$H_7SiV_3W_9O_{40}$-TiO_2	93.4	68.1
6	$[C_{16}H_{33}N(CH_3)_3]_7SiV_3W_9O_{40}$-$TiO_2$	98.2	71.3

[a] Condition for demercaptanization: 5 mL of the model sulfur compound, mixed with 2 mL H_2O_2. The flask was immersed in the heating bath and stirred at 500 rpm for 1 hour.