Highly catalytic oxidative desulfurization and denitrogenation of diesel using anchored-silica-gel vanadium-substituted Dawson-type polyoxometalate

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Abstract

The aim of this article is to study the extractive-catalytic oxidative desulfurization (ECODS) of the model oil containing several model S-containing compounds as well as N-containing compound using a heterogeneous vanadium substituted Dawson-type polyoxometalate catalyst under atmospheric pressure and temperature lower than 100 °C. The catalyst was prepared by ion exchange with alkyl ammonium derivatives covalently anchored to silica gel. The potential of this methodology was illustrated by oxidation of 100% quinoline and 80% of total sulfur in model oil containing 500 ppmw sulfur and 70% of total sulfur in model oil 1500 ppmw in less than 30 minutes of reaction, in the absence of solvent. However, when acetonitrile was employed as an extractive solvent, the desulfurization was increased considerably. Under the reaction conditions, activated catalyst and acetonitrile, solvent to oil ratio 1:6, could remove approximately 100% of quinoline, 95% of sulfur from 500-ppmw model oil, 87% of sulfur from 1500-ppmw model oil in less than 30 min. The catalyst is very active in ECODS and can be reused fifth times from 500-ppmw model oil and third times from 1500-ppmw model oil without an important decrease in activity. The ECODS could remove 83% of total sulfur from 1235-ppmw-S real diesel.

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1. Introduction

Sulfur removal from fuel oil has gained significant attention due to the global environmental awareness about the serious consequence of burning sulfur-bearing fuels. Environmental protocols in this regard become stricter day by day [1, 2]. There are various techniques for the desulfurization of oil fuels such as selective adsorption, extractive separation, hydrodesulfurization (HDS) and oxidative desulfurization (ODS) [3-14]. Among various desulfurization methods, HDS is considered as a common and practical method for sulfur removal in the petroleum refineries [1, 2]. While to achieve ultra-low sulfur content fuel oil, typical HDS requires more severe conditions such as higher temperature, pressure, hydrogen consumption and large residence time which impose higher operating cost [1-4]. ODS has been confirmed to be one of the most promising and favorable alternative desulfurization processes to achieve ultra-low sulfur content fuels [1-14]. Desulfurization under mild conditions (temperature lower than 100 °C and atmospheric pressure) in the liquid phase is the utmost advantage of ODS as compared to the conventional HDS. In the ODS reaction, sulfur compounds can be oxidized by the electrophilic addition and then will be removed by a solvent [4-8]. In the ODS process, H_2O_2 is the mostly selected oxidant, because its byproduct is water [1-14]. Several kinds of catalysts have been used in the bipolar liquid-liquid ODS system in the presence of H_2O_2 .

In our previous works [1-3], we have shown that an emulsion catalyst acting as a phase transfer agent in the ODS system can be very effective. However, the main problems for these kinds of catalyst are the difficulties in recovery and reusability. Therefore, the use of supported catalysts in ODS processes has been more considered in recent years. Various types of supported catalysts have been studied in the ODS system [4-14] such as $\text{MO}_x/\text{Al}_2\text{O}_3$

[4], Titanium supported catalyst [9]. However, their selectivity for oxidized sulfur compounds is not enough, and some other components are also oxidized [9-14]. Hence, the new type of supported catalysts with high selectivity should be considered in heterogeneous ODS of fuel. Among various catalysts, used together with H_2O_2 , polyoxometalate (POM or Hetero Poly Acid (HPA)) has been more suggested due to the several advantages such as high selectivity and its potential for desulfurization of satirically hindered sulfur compounds. Furthermore, it is an environmentally friendly catalyst [1-3]. Two common types of POMs, Keggin-type and Dawson-type, were used in oxidation process. Although Keggin-type POMs have gradually become worldwide popular for ODS application [15-20]; few studies paid attention to ODS by Dawson-type POMs. One of the most important subclasses of POM is the vanadium (V) substituted POMs. In fact, V^{n+} is the most strongly oxidizing element and can be readily reduced to $\text{V}^{(n-1)+}$ with concomitant oxidation of an organic substrate. The addition of vanadium is useful to shift POM's reactivity from acid-dominated to redox-dominated, as demonstrated by the oxidation of some organic compounds [1-3]. Some authors have been tried to synthesize supported POM catalyst by immobilization on a silica functionalized alkyl ammonium salts [4-14].

In this work, in continuation of our previous works [1-6] and in order to overcome the problem of reusability of the POM catalyst, the ODS of model oil containing several model S-containing compounds (benzothiophene (BT), dibenzothiophene (DBT) and 4, 6 di-methyl dibenzothiophene (4, 6 DMDBT)) and quinoline (Q) as a model N-containing compound has been studied using a new type of silica (functionalized alkyl ammonium salts) supported polyoxometalate catalyst.

2. Experimental

2.1. Catalysis preparation

The vanadium substituted Dawson-type phosphotungstate heteropoly acid, $\text{H}_{11}\text{P}_2\text{W}_{13}\text{V}_5\text{O}_{62}$ was synthesized based on our previous works [1-3]. The 0.033 mole ammonium monovanadate and 0.08 mole sodium phosphate were dissolved in 100 mL deionized water at 40 °C. Thereafter, 0.017 mole sodium tungstate was added, and the pH was adjusted to 4.4 by adding a certain amount of sulfuric acid (1 mol/L), then the solution was refluxed for 8 hours. The solution was allowed to cool slowly to room temperature. Then, 150 mL diethyl ether was added, and the mixture was shaken and allowed to separate for 1 hour. The solution was divided into three phases; the red substance at the bottom was a mixture of heteropoly acid and diethyl ether. After evaporation of diethyl ether and drying at 200 °C, a powdered well-Dawson vanadium substituted heteropoly acid was obtained.

The heterogeneous catalyst were synthesized by ionic exchange of quaternary ammonium functionalized silica (Silicycle: SiliaBond[®] TMA Chloride). An excess (3:1) of heteropoly acid was solubilized in water (25 mL), and then 4 g of support was added. The mixture was stirred overnight. The solid was filtered off and washed with demineralized water and dried at 75 °C in vacuum oven.

2.2. Catalyst characterization

The metal content of the synthesized catalyst was determined using X-ray fluorescence (XRF) spectroscopy using an ARL analyzer with an Rh anode of an X-ray tube and VRA analyzer with a Cr anode of an X-ray tube. Fourier transform infrared (FT-IR) was used to confirm the formation of a Dawson-type structure. FT-IR spectra were recorded on a Shimadzu-8400S FT-IR spectrometer using 3 wt. % KBr pellets. Ultraviolet-visible diffuse reflectance spectroscopy (UV-vis DRS) was recorded on a Varian Cary 5000 UV-vis spectrophotometer equipped with an integrating sphere to distinguish the electronic properties of the center-metal ions. The BaSO_4 was used as the internal standard. X-ray photoelectron (XPS) spectrum was obtained by using VG Escalab 200 R with Al/Mg X-ray source. Pass

energy was 20 eV and base pressure of analysis chamber was not greater than 1×10^{-8} Pa. The spectra were calibrated against the reference binding energy of C 1s (284.8 eV). Thermogravimetric-differential thermal analysis (TGA) was done using TA-Q500 instrument from room temperature to 600 °C under pure nitrogen environment at a heating rate of 5 °C/min.

2.3. Catalyst activity test

Two kinds of model diesel were used in this study. The 500 ppmw sulfur containing model oil, named as 500-ppmw-S model oil, contained approximately 646 ppmw BT, 1493.8 ppmw DBT, 646 ppmw 4, 6-DMDBT and 445 ppmw quinoline in the 2, 2, 4-trimethyl pentane containing 20 v.% toluene. The second one included 1500 ppmw sulfur (2650 ppmw BT, 6150 ppmw DBT, 2650 ppmw 4,6-DMDBT) as well as 1335 ppmw quinoline in the 2, 2, 4-trimethyl pentane containing 20 v.% toluene. In addition to model oil, the performance of new catalyst has been study in real diesel containing 1235 ppmw sulfur kindly provide by CEPSA (Spain).

The optimized conditions, determined in our previous works [1-4], have been used in this study. In a typical ODS run, the solution was heated to 60 °C. The 7.5 g/L supported catalyst and the oxidant, 50 wt. % H_2O_2 (mole ratio of oxidant to oxidized agent, 4) were added to the solution simultaneously at a magnetic stirring speed of 1000 r/min. In a typical extractive oxidative desulfurization (ECODS) run, the mixture, containing model oil and acetonitrile as an extractor (solvent to oil ratio, 1:6) was heated to 70 °C. The 7.5 g/L supported catalyst and the oxidant, 50 wt. % H_2O_2 (mole ratio of oxidant to oxidized agent, 4) were then added to the mixture simultaneously at a magnetic stirring speed of 1000 r/min. The sample was taken in the different time and put into an ice chamber to stop the reaction. The catalyst and solvent in the sample were separated by decantation. The performance of reaction was analyzed by a gas chromatography (Agilent, 7890A) coupled with a FID detector using a capillary column (HP-5, 30m $\times$ 0.32mm $\times$ 0.25 μ m).

The ECODS of real diesel was run same as model oil under the optimum conditions. After each run, the oil phase was separated by decantation. The sulfur content in real diesel after reaction was determined using X-ray fluorescence spectrometer (ASTM D4294 method).

3. Results and discussions

3.1. Catalyst characterization of supported catalyst

The metal content of catalyst was determined by XRF analysis. The results demonstrated that the supported catalyst, PWV5/TMA-Si, contained 27.27 wt. % metal content (24.9 wt. % tungsten, 2.37 wt. %).

Fig. 1(a) and (b) shows the FT-IR pattern of supported catalyst and the comparison between FT-IR patterns of supported catalyst and polyoxometalate patterns. These figures illustrates that new peaks has been appeared in region between 780 to 1100 cm^{-1} . They are related to vanadium substituted Dawson type POM on the surface of functionalized silica. Other peaks are related to quaternary ammonium (1447- 1468 cm^{-1} and 2333- 2360 cm^{-1}) and hydroxide group ($\sim 3442 \text{ cm}^{-1}$) [1-6].

The DRS-UV-vis spectrum of PWV5/TMA-Si demonstrates absorptions associated with the ligand metal charge transfer (LMCT) from the oxygen to the transition metal ion of POM (Fig. 2). PWV5/TMI-Si spectrum shows two absorption band at 257 and 355 nm, which is characteristic of vanadium-substituted Dawson-type polyoxometalate. The first one is assigned to LMCT from oxygen to phosphorous and tungsten. The second one is attributed to LMCT from oxygen to vanadium [1-4].

The binding energies of V2p (V2p_{3/2}: 517.08 eV, V2p_{1/2}: 524.11 eV) and W4f (W4f_{7/2}: 35.23 eV, W4f_{5/2}: 37.12 eV) in XPS pattern of PWV5/TMA-Si (Figs. 3 (a) and 3(b)) indicate that the ions remain in the highest oxidation state [1-4].

Summing up, all data obtained from FT-IR, UV-DRS-vis and XPS analysis approved that the supported catalyst has been synthesized successfully.

TGA analysis shows three weight loss (Fig. 4). The first one is related to coordinated water. The two next ones are attributed to the decomposition of vanadium-substituted POM and tri-methyl-propyl ammonium group [2-3].

3.2. Performance of catalyst

The blank tests were done to find out the performance of ODS and EODS of both model oils, 500-ppmw-model oil and 1500-ppmw-model oil, in the absence of the new supported catalyst. Figures 5 and 6 reveal that the efficiency of both ODS and EODS of 500-ppmw-model oil and 1500-ppmw-model oil were not enough to achieve ultra-low sulfur containing (ULS) fuels. Therefore, in continuous, the new supported catalyst was used in both ODS and EODS process. The presence of catalyst improved the efficiency of ODS and EODS of model oils. The catalytic oxidative desulfurization (CODS) was able to remove 100 % of quinoline from both model oils. CODS achieves around 80% removal of sulfur from 500-ppmw-model oils (Fig. 7(a)). The increase in sulfur content of model oil from 500 ppmw to 1500 ppmw decreased efficiency of system around 12.5% (Figs. 7(a) and 7(b)). In order to improve the efficiency of desulfurization of fuels, acetonitrile was used simultaneously by the new supported catalyst (Figs 8(a) and 8(b)). Extractive-catalytic oxidative desulfurization (ECODS) was able to remove 95% of sulfur and 100% of quinolone from 500-ppmw-model oil after less than 30 minutes. The increase in sulfur content of model oil reduced the efficiency of system same as its negative effect on the CODS process. The new ECODS could reduce the sulfur content of system from 1500 ppmw to about 195 ppmw after less than 30 minutes. It could be achieved ULS diesel by repeat ECODS process.

The reusability of ECODS was also studied. Fig. 9(a) demonstrates that the new ECODS system containing PWV5/TMA-Si had a good reusability. It could be reused 5 times with negligible activity lost and loss of catalyst after each run. The increase in sulfur content

reduced reusability of catalyst. The new ECODS could be reused three times with the low activity lost from 1500-ppmw-model oil (Fig. 9(b)).

The performance of new ECODS was also studied for real diesel oil (Fig. 10). The results showed that it could reduce the sulfur content of 1235-ppmw-S real diesel oil to below 200 ppmw. The reusability of new ECODS of real fuel was good. It could be reused three times without a significant decrease in activity and treatment after each recycle steps. The result also revealed that the important loss of catalyst was not seen during the recycle runs.

The activity lost after several recycle runs can be referred to catalyst loss during recycling and blockage of catalyst surface. The XPS analysis also showed that binding energy of V2p_{3/2} peaks were pretty constant around 517-516 eV that indicate no change in the oxidation state of the vanadium from fresh to after 1st run after 5th run respectively (Fig 11(a)).

The transformations of peaks of W4f_{7/2} from 35.2 eV (Fresh system) to 35.7eV (1st and 5th runs) were attributed to the formation of peroxometalates moieties with hydrogen peroxide in organic solution (Fig. 11(b)). So, it was found out that tungstate took a main role in transfer of oxygen from H₂O₂ to S/N-compounds selectively and catalyzed the ECODS process [1-4]. We detect a decrease in the signal intensity of the peaks of V and W after reaction, but the Surface atomic ratio V/Si and W/Si did not change significantly. This finding indicates that surface of the catalyst can be covered by organic compounds.

4. Conclusions

For the first time, ECODS of several model S-containing compounds (BT, DBT and 4, 6 DMDBT) and quinoline as a nitrogen containing compound from model oil and real diesel oil using new kinds of supported catalyst was studied. The selected solvent used to synthesize model oil was quite realistic because it had a 1-ring aromatic compound (20 v. % toluene in iso-octane) that made the process difficult. In order to overcome initial water content of system, the oxidant employed was 50 wt. % hydrogen peroxide (mole ratio oxidant to

oxidized agents, 4). The new supported catalyst, synthesized by ion-exchanged, was a vanadium-substituted Dawson-type polyoxometalate tethered on silica functionalized by trimethyl-propyl ammonium groups (TMA-Si). The heterogeneous catalyst was tested using soft reaction conditions: temperature range below 100 °C and atmospheric pressure. The new supported catalyst was able to activate selectively hydrogen peroxide to oxidize S/N compounds via transfer of tungsten to peroxometalate. The potential of this methodology was illustrated by ~ 80% oxidation of total sulfur in 500-ppmw model oil and ~ 70% oxidation of total sulfur in 1500-ppmw model oil after lower than 30 minutes, in the absence of a solvent. However, when acetonitrile was employed as extractor solvent; the desulfurization efficiency was increased clearly. Under the reaction conditions Activated PWV5/Si-TMA and acetonitrile as a solvent, ratio solvent to oil 1:6, was able to remove approximately 95 % of sulfur from 500-ppmw model oil and more than 80 % of sulfur from 1500-ppmw model oil. The activated PWV5/Si-TMA catalyst was very active in ECODS reaction and could be reused five times without loss of activity from 500-ppmw model oil. The performance of new ECODS of 1235-ppmw real diesel oil was also demonstrated by ~83% removal of sulfur compound and 3-time reusability without an obvious decrease in activity.

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Figure Captions

Fig.1. (a) FT-IR patterns of supported catalyst, $H_{11}P_2W_{13}V_5O_{62}/TMA-Si$, (b) Comparison between FT-IR spectrum of TMA-Si and supported catalyst.

Fig. 2. UV spectrum of supported catalyst, $H_{11}P_2W_{13}V_5O_{62}/TMA-Si$.

Fig. 3. XPS spectrum of (a) V2p and (b) W4f.

Fig. 4. TGA analysis of $H_{11}P_2W_{13}V_5O_{62}/TMA-Si$.

Fig. 5. Blank activity test of 500-ppmw-model oil at 70 °C (a) Only oxidizer, 50 wt.% H_2O_2 , mole ratio of oxidizer to oxidized agent =4, (b) Only oxidizer, 50 wt. % H_2O_2 , and acetonitrile, solvent to oil volume ratio = 1:6.

Fig. 6. Blank activity test of 1500-ppmw-model oil at 70 °C (a) Only oxidizer, 50 wt.% H_2O_2 , mole ratio of oxidizer to oxidized agent =4, (b) Only oxidizer, 50 wt. % H_2O_2 , and acetonitrile, solvent to oil volume ratio = 1:6.

Fig. 7. One-pot catalytic oxidative desulfurization of (a) 500-ppmw-model oil and (b) 1500-ppmw-model oil (oxidizer, 50 wt.% H_2O_2 , mole ratio of oxidizer to oxidized agent, temperature 70 °C, catalyst dosage ,7.5 g/L).

Fig. 8. One-pot extractive-catalytic oxidative desulfurization of (a) 500-ppmw-model oil and (b) 1500-ppmw-model oil (oxidizer, 50 wt.% H_2O_2 , mole ratio of oxidizer to oxidized agent, acetonitrile as a extractor solvent, solvent to oil volume ratio = 1:6, temperature 70 °C, catalyst dosage ,7.5 g/L).

Fig. 9. Reusability of extractive-catalytic oxidative desulfurization of (a) 500-ppmw-model oil and (b) 1500-ppmw-model oil without any treatment after each run (oxidizer, 50 wt.% H_2O_2 , mole ratio of oxidizer to oxidized agent, acetonitrile as a extractor solvent, solvent to oil volume ratio = 1:6, temperature 70 °C, catalyst dosage ,7.5 g/L, time: 30 min).

Fig. 10. Reusability of extractive-catalytic oxidative desulfurization of diesel fuel without any treatment after each run (oxidizer, 50 wt.% H_2O_2 , mole ratio of oxidizer to oxidized

agent, acetonitrile as a extractor solvent, solvent to oil volume ratio = 1:6, temperature 70 °C, catalyst dosage ,7.5 g/L, time: 30 min).

Fig. 11. XPS spectra of (a) V2p of fresh catalyst and after 1st and 5th runs and (b) W4f of fresh catalyst and after 1st and 5th runs.

(a)

(b)

Fig.1. (a) FT-IR patterns of supported catalyst, $H_{11}P_2W_{13}V_5O_{62}/TMA-Si$, (b) Comparison between FT-IR spectrum of TMA-Si and supported catalyst.

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(a)

(b)

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(a)

(b)

Fig. 6. Blank activity test of 1500-ppmw-model oil at 70 °C (a) Only oxidizer, 50 wt.% H_2O_2 , mole ratio of oxidizer to oxidized agent =4, (b) Only oxidizer, 50 wt. % H_2O_2 , and acetonitrile, solvent to oil volume ratio = 1:6.

(a)

(b)

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(a)

(b)

Fig. 8. One-pot extractive-catalytic oxidative desulfurization of (a) 500-ppmw-model oil and (b) 1500-ppmw-model oil (oxidizer, 50 wt.% H_2O_2 , mole ratio of oxidizer to oxidized agent, acetonitrile as a extractor solvent, solvent to oil volume ratio = 1:6, temperature 70 °C, catalyst dosage ,7.5 g/L).

(a)

(b)

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(a)

(b)

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