Synthesis and Application of Dawson-Type Vanadium Polyoxotungstate Emulsion Catalyst for Oxidative Desulfurization

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Abstract

Environmental pollutions originated from fossil fuel cause to consider the development of rigorous rules to remove sulfur containing compounds and achievement of novel process to follow the mentioned rigorous rules. In this regard and for the first time, new Dawson-type vanadium polyoxotungstate emulsion catalysts, [TBA]_{6+x}P_2W_{18-x}V_xO_{62} (x= 0, 1, 3, 5) have been synthesized successfully for oxidative desulfurization of sulfur compounds and characterized by using element analysis, FTIR, 31P MAS NMR and UV-vis DRS. These catalysts were used to oxidize sulfur-containing components, dibenzothiophene and benzothiophene by using hydrogen peroxide under mild conditions (temperature lower than 100 °C and atmospheric pressure). The activity of catalysts has been grown by an increase in the number of vanadium, in the structure of heteropoly anion. The reactivity of sulfur compound, dibenzothiophene was much more than benzothiophene. The emulsion catalyst with the highest number of vanadium, [TBA]_{11}P_2W_{13}V_5O_{62}, could oxidize 85% of dibenzothiophene and 50% benzothiophene after 75 minutes, under temperature 60 °C and by using hydrogen peroxide 30 v-% in oxygen to sulfur mole ratio 4.

Keywords: Catalytic-Oxidative Desulfurization, Dawson-type Polyoxometalate, Emulsion Catalyst, Vanadium, Tetrabutyl Ammonium.
Introduction
The desulfurization of fuel oil becomes more important because of the environmental concerns about the thoughtful consequences of pollution caused by burning of fossil fuel [1]. Among different desulfurization methods to achieve ultra-low sulfur content liquid fuel, oxidative desulfurization (ODS) can be an acceptable and promise sulfur-removal to remove aromatic sulfur-containing compound such as dibenzoiiophene and benzothiophene [2, 3]. ODS can remove aromatic sulfur content by oxidation of them to sulfones and sulfoxides under mild conditions (temperature lower than 100 °C and atmospheric pressure) in the liquid phase by means of strong and environmental friendly oxidant such as H$_2$O$_2$ [4, 5]. Among various catalysts, used together with H$_2$O$_2$, polyoxometalate (POM) has been more drawn attention due to its potential for desulfurization of satirically hindered sulfur compounds [6].

POM is an oxygenated polybasic acid which can be classified in the two significant types: Keggin-type ([XM$_{12}$O$_{40}$]p- X=P or Si, M=Mo or W) and Dawson-type ([XM$_{18}$O$_{62}$]p-, X=P or Si, M=Mo or W) [7]. The most of previous works on desulfurization are restricted to Keggin-type catalyst, while the Dawson type POM has been studied in desulfurization less [8-10]. Dawson-type POM demonstrates more selectivity and activity in oxidation reaction than Keggin-type POM [10]. One of the most significant sub-groups of POM is the vanadium (V) substituted POMs. The presence of vanadium in POM cage shifts reactivity to redox-dominated, as demonstrated by the oxidation of some organic compounds [8-10]. In order to overcome to phase transfer resistance between aqueous phase and the oil phase, POM catalyst has been modified by using phase transfer agent. It help to achieve POM-based hybrid catalysts with higher catalytic efficiency, recovery and reusability capacity [8-12].

Although Keggin-type hybrid POMs have progressively become widespread for ODS application [1-12]; few studies paid attention to ODS by Dawson-type POMs. So, in this study, a series of Dawson-type vanadium substituted phosphopolyoxotungstate emulsion catalysts, Q$_{6-x}$P$_x$W$_{18}$O$_{62}$ (tetra-n-butyl ammonium (TBA) and x= 0, 1, 3, 5) were prepared and characterized. They were used for oxidative desulfurization of model diesel.

Methodology
All reagents were available commercially and were used without further purification. The model sulfur containing compounds including benzothiophene (BT) and dibenzothiophene (DBT) and all chemical agents such as solvent (iso-octane) and 30 wt. % hydrogen peroxide were obtained from Sigma-Aldrich.

The potassium salts, K$_6$[P$_2$W$_{18}$O$_{62}$] and K$_{10}$[P$_2$W$_{17}$O$_{61}$], were synthesized using the Randall’s method and heteropoly acid, H$_6$$^+$x(P$_2$W$_{18}$-xVxO$_{62}$), (x=1, 2, 3) were synthesized using etherate method [10, 11]. To synthesize of Emulsion catalyst TBA$_{6-x}$P$_x$W$_{18}$V$_x$O$_{62}$, (x=1, 2, 3), one of heteropoly acid (0.2-0.22 mole) was dissolved in 15 to 30 mL deionized water. The pH of solution was set between 3 and 4 by means of 4-molar hydrochloric acid. Then, aqueous heteropoly acid solution was added to solution containing 2-2.2 mole of TBA salt slowly. The produced deposition was achieved after two hours. The deposition was separated by using
centrifuge and dried in 70 °C vacuum oven overnight. Fourier transform infrared (FT-IR) spectra were measured using a Shimadzu-8400S FT-IR spectrometer using 3 wt. % KBr pellets. Elementary analysis was determined using ECS 4010 CHNS-O elemental analyzer, Costech Analytical Technologies, Inc., Italy and Inductively Coupled Plasma Spectroscopy ICP (ICPS S7000, Shimadzu). UV-vis diffuse reflectance spectroscopy (UV-vis DRS) was determined on a Shimadzu UV-2101 PC spectrometer equipped with a diffuse-reflectance to distinguish the electronic properties of the center-metal ions. The BaSO₄ was used as the internal standard. The BaSO₄ samples were placed in the spectrometer and scanned from 190 to 800 nm in a step-scan mode with a step of 2 nm. High-power proton decoupling ³¹P MAS NMR spectra were performed on a NMR spectrometer BRUKER AVANCE II-9,4 Tesla magnet (400MHz) operating at 162 MHz with a MAS probe-head using 4-mm ZrO₂ rotors spun at 10 kHz. The recording parameters were 2.0 μs pulse, 2-second repetition time, and 2048 scans. The 31P chemical shift was normalized with 85% H₃PO₄ aqueous solution.

The ODS studies were performed on a model diesel containing representative refractory sulfur compounds in diesel: approximately 500 ppmw DBT and 500 ppmw BT in 2, 2, 4-trimethylpentane. The solution was heated to 60 °C. The emulsion catalysts (10 g/L) and the oxidant H₂O₂ (aqueous phase, 30 wt.%, mole ratio of Oxygen (O): Sulfur (S) =4) were added to the above sulfur-containing solution simultaneously at a magnetic stirring speed of 1000 r/min. The sample was taken after 60 min and put into an ice chamber to stop the reaction. The catalyst in the emulsion sample was separated by centrifugation. The performance of reaction was analyzed by a gas chromatography (Agilent, 7890A) coupled with a FID detector using a capillary column (HP-5, 30m×0.32mm×0.25μm).

**Discussion and Results**

The elemental analyses of the emulsion catalysts and the vanadium-substituted heteropoly anion acids illustrated that the experimental values are approximately similar to the calculated values. These data suggest that the emulsion catalysts prepared are similar to expected ones. The FT-IR spectra of TBA₆+xP₂W₁ₓVₓO₆₂ (x= 0, 1, 2, 3) and TBA₁₀P₂W₁₇O₆₁ shows strong evidence for the vanadium substituted Dawson-type emulsion catalyst (W, P). The P=O band between 1080-1090 cm⁻¹ indicates the retention of the basic Dawson-type framework compared with their corresponding potassium salts and heteropoly acids. Moreover, the band at 1468 cm⁻¹ is referred to deformation vibrations of the C-H which belongs to CH₃ and CH₂. The asymmetric stretching vibrations of C-H are found 2958 cm⁻¹. The symmetric stretching vibrations of C-H are at 2870 cm⁻¹ which result from the CH₃ and CH₂ in the TBA cations. FT-IR results have showed that the quaternary ammonium cations and polytungstophosphate anions effectively combine with each other by electrostatic interactions [12]. The strong and broad FT-IR bands around 3420-3442 cm⁻¹ are for O-H vibrations. It is indicative of the hydrogen bonding networks among polyoxometalate anion and quaternary ammonium counter cation [13]. The UV spectra of catalysts exhibits the absorption bands at 198, 214, 278 and 378 nm, attributed to the Dawson-type structure and in
the solid-state shows the line with resonance at -13.75 ppm was related to Dawson-type anion \([P_2W_{18}]^-\)6 while the peaks at -6.617 ppm and -14.28 ppm were due to the presence of Dawson-type anion \([P_2W_{17}]^-\)10. The vanadium substituted Dawson-type heteropoly acids and vanadium substituted emulsion catalysts have showed a peak at -13.5 ppm which is typical of vanadium substituted Dawson-type POM. The peak around -10.42 ppm related to the substitution of tungstate by vanadium was omitted by the increase the number of vanadium in frame of POM. The peak with resonance -13.5 ppm becomes intense by increase the amount of vanadium in frame of POM. Summing up, 31P MAS NMR analysis also indicate that the Dawson structure was reserved in all samples, and indicates the introduction of vanadium in frame of POM [13].

The oxidation of DBT (500 ppmw) and BT (500 ppmw) was performed using hydrogen peroxide (30 wt.%) (Molar ratio Oxygen (O): Sulfur(S) =4) in the presence of Dawson-type vanadium-substituted emulsion catalysts under mild (60 °C and atmospheric pressure) and a two phase (aqueous-octane) reaction conditions, without any additional solvent. Sulfur compounds conversion increases with time and reaches a plateau after 75 minutes of reaction (Figures 1 (a) 4(b)), that corresponds to 90% for DBT and 76% for BT for the studied reaction. Reaction termination can be referred to the competition between the hydrogen peroxide decomposition side reaction and sulfur-containing compounds (DBT, BT) oxidation reaction [8-12]. A comparison of the reaction results shows that oxidation reactivity of the sulfur compounds was different and follow the order DBT> BT, indicating that DBT can be more easily oxidized than BT at the reaction conditions used in this work, in opposition the hydro treatment (HDS) reactivity [8-12]. The higher reactivity of the DBT compared to BT can be explained by the electron densities on sulfur atoms, (5.758 for DBT and 5.739 for BT) [8-12]. Figure 1 shows that emulsion catalysts (with two kinds of coordination atoms V and W) is higher than that of emulsion catalysts with one coordination atoms W. Their catalytic activity is in the order of V5>V3>V1. It is possible that the Dawson-type heteropoly anion is easily formed by self-assembly when two catalyst precursors are mixed. The catalytic performance corresponds to the reduction potential with respect to vanadium substitution. The substitution of W6+ with V5+ results in the generation of more reactive lattice oxygen associated to the W-O-V species [8-12]. It can be say that the oxidation-reduction of vanadium substituted Dawson-type mainly depends on V atom, and comes from the change between vanadium-V and vanadium-IV. agreement with the results reported previously [13]. 31P MAS NMR spectra emulsion catalysts in

Figure 1. Conversion of BT and DBT vs. Time (60 °C. The emulsion catalysts (10 g/L), the oxidant \(H_2O_2\) (aqueous phase, 30 wt.%, mole ratio of Oxygen (O): Sulfur (S) =4)
Conclusions

In summary, amphiphilic vanadium substituted Dawson-type phosphotungstate emulsion catalysts, $\text{TBA}_{6+x} \text{P}_2\text{W}_{18-x}\text{V}_x\text{O}_{62}$ ($x = 0, 1, 3, 5$), were successfully synthesized and characterized. The characterization showed that emulsion catalysts retain the Dawson-type structure of the tungestovanadophosphoric anion with quaternary ammonium cations. Different vanadium-substituted polyoxometalate hybrid catalysts, $\text{TBA}_{6+x} \text{P}_2\text{W}_{18-x}\text{V}_x\text{O}_{62}$ ($x = 0, 1, 3, 5$), was used in the oxidation of sulfur compounds in model diesel (approximately 500 ppmw DBT and 500 ppmw BT) in iso-octane. This is the first time that this kind of catalysts was prepared and used for this application. The results showed that the oxidative desulfurization of DBT and BT increases by increasing the number of vanadium substitution.

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References


