

# Ultra-deep Oxidative Desulfurization of Fuel Oil Catalyzed by Dawson-type Polyoxotungstate Emulsion Catalysts

ZHANG Yongna<sup>1,2</sup>, WANG Lu<sup>1,2</sup>, ZHANG Yuliang<sup>1,2</sup>, JIANG Zongxuan<sup>1,#</sup>, LI Can<sup>1,\*</sup>

<sup>1</sup>State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, Liaoning China

<sup>2</sup>Graduate University of Chinese Academy of Sciences, Beijing 100049, China

**Abstract:** The Dawson-type polyoxotungstate emulsion catalysts  $Q^{18}P_2W_{18}$ ,  $Q^{18}P_2W_{17}$ , and  $Q^{18}P_2W_{12}$  were successfully synthesized and characterized by IR and  $^{31}P$  MAS NMR. They were used for the oxidation of sulfur-containing compounds such as 4,6-dimethyldibenzothiophene (4,6-DMDBT), dibenzothiophene (DBT), benzothiophene (BT), and 2,5-dimethylthiophene (2,5-DMT) with  $H_2O_2$  as an oxidant under mild conditions. The activity of the catalysts decreased in the order:  $Q^{18}P_2W_{12} > Q^{18}P_2W_{17} > Q^{18}P_2W_{18}$ . The oxidative reactivity of the sulfur-containing compounds decreased according to  $DBT > 4,6-DMDBT > BT > 2,5-DMT$ . BT was completely oxidized into the corresponding sulfone upon catalysis by  $Q^{18}P_2W_{12}$  at 60 °C for 30 min.

**Key words:** Dawson-type; polyoxotungstate; emulsion catalyst; oxidative desulfurization

The removal of sulfur in fuel oils is becoming a worldwide challenge because of increasingly stringent environmental regulations. In the petroleum refining industry, hydrodesulfurization (HDS) is a conventional method for the removal of sulfur compounds [1–3]. However, some refractory sulfur compounds such as 4,6-dimethyldibenzothiophene (4,6-DMDBT) and its derivatives are removed with difficulty because of steric hindrance. To achieve ultra-deep desulfurization through typical HDS more severe conditions are required such as higher temperature, higher hydrogen pressure, and catalysts with higher activity. These factors inevitably lead to a higher operating cost. Oxidative desulfurization (ODS) has been demonstrated to be a promising alternative because of its mild operating conditions and no hydrogen being required [4]. During this process, the sulfur-containing compounds in the fuels are easily oxidized into sulphones, which can be removed in the later extraction process using water-soluble polar solvents as the extractants [5].

Various studies on the ODS process have used different catalysts such as zeolitic titanosilicates [6–8], metal oxide catalysts [9], and polyoxometalates (POMs) [10–13]. In our

previous work, we reported several quaternary ammonium polytungstophosphate emulsion catalysts for the oxidation of the sulfur-containing compounds present in fuel oils [14–16]. It is not necessary to add organic acids, polar extractants, or polar solvents to the reaction system. Furthermore, these catalysts can improve the formation of an emulsion and thus increase the reaction efficiency between the sulfur-containing compounds and hydrogen peroxide. The Keggin-type lacunary polyoxotungstate catalyst shows higher catalytic activity toward the oxidation of sulfur-containing compounds in the emulsion [16]. However, few studies paid any attention to catalysis by POMs with a Dawson-type structure during oxidative desulfurization.

Herein, a series of Dawson-type polyoxotungstate catalysts,  $Q^{18}P_2W_{18}$ ,  $Q^{18}P_2W_{17}$ , and  $Q^{18}P_2W_{12}$ , were prepared and used for the oxidation of sulfur-containing compounds.

$K_6[P_2W_{18}O_{62}] \cdot 14H_2O$ ,  $K_{10}[P_2W_{17}O_{61}] \cdot 20H_2O$ , and  $K_{12}[\alpha-H_2P_2W_{12}O_{48}] \cdot 24H_2O$  were prepared using the method described in the literature [17]. These salts (0.21–0.22 mmol) were dissolved in distilled water (15–30 ml) properly followed by adjusting the pH with a solution of HCl (4 mol/L), respec-

Received 29 November 2010. Accepted 29 December 2010.

\*Corresponding author. Tel: +86-411-84379070; Fax: +86-411-84694447; E-mail: canli@dicp.ac.cn

#Corresponding author. Tel: +86-411-84379990; Fax: +86-411-84694447; E-mail: zxjiang@dicp.ac.cn

**Foundation item:** Supported by the National Basic Research Program of China (973 Program, 2006CB202506) and the National Natural Science Foundation of China (20673114).

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DOI: 10.1016/S1872-2067(10)60170-2

tively. Then a solution of octadecyltrimethylammonium chloride (CTAC) (2.1–2.2 mmol) that was dissolved in alcohol (10 ml) was added dropwise. An azure or white precipitate was immediately formed. After continuous stirring for 1 h, the resulting mixture was filtered and dried at 60 °C in vacuum for 12 h to give  $Q^{18}P_2W_{18}$ ,  $Q^{18}P_2W_{17}$ , and  $Q^{18}P_2W_{12}$ , respectively.

High-power proton decoupling  $^{31}P$  MAS NMR spectra were performed on a Bruker DRX 400 spectrometer operating at 161.8 MHz with a BBO MAS probe-head using 4-mm  $ZrO_2$  rotors spun at 10 kHz. The recording parameters were 2.0  $\mu$ s pulse, 2 s repetition time, and 2048 scans. The  $^{31}P$  chemical shift was normalized with 85%  $H_3PO_4$  aqueous solution. Fourier transform infrared (FT-IR) spectra were recorded on a Nicolet 470 FT-IR spectrometer. The samples were diluted with KBr and pressed into a pellet.

A typical catalytic activity test proceeded as follows. 2,5-Dimethylthiophene (2,5-DMT), benzothiophene (BT), dibenzothiophene (DBT), or 4,6-DMDBT (0.39 mmol) was dissolved in a solution of decalin (12.5 ml) in a 60 °C oil bath to quantify the sulfur content as 1000 ng/ $\mu$ l. The catalysts  $Q^{18}P_2W_{18}$ ,  $Q^{18}P_2W_{17}$ , or  $Q^{18}P_2W_{12}$  (0.0044 mmol) and the oxidant  $H_2O_2$  (0.14 ml, 30%) were added to the above sulfur-containing solution simultaneously at a magnetic stirring speed of 1000 r/min. The immediate formation of a turbid W/O emulsion was observed. To follow the reaction, the emulsion was sampled at time intervals of 1 h and stored in an icebox to quench the reaction. The catalyst in the sampled emulsion was separated from the emulsion phase by centrifugation. The content of sulfur in the oil was determined by a gas chromatography (Agilent 6890N) coupled with a flame photometry (FPD, Agilent H9261) using a capillary column (PONA, 50 m  $\times$  0.2 mm  $\times$  0.5  $\mu$ m).

The  $^{31}P$  MAS NMR spectra in the solid-state show a one-line spectrum with a resonance at  $\delta = -13.2$  for  $Q^{18}P_2W_{18}$  (shown in Fig. 1(1)), a two-line spectrum with resonances at  $\delta = -8.8$  and  $-13.7$  for  $Q^{18}P_2W_{17}$  (shown in Fig. 1(2)), and a one-line spectrum with a resonance at  $\delta = -8.8$  for  $Q^{18}P_2W_{12}$  (shown in Fig. 1(3)). These results agree with that in the literature [17–19].

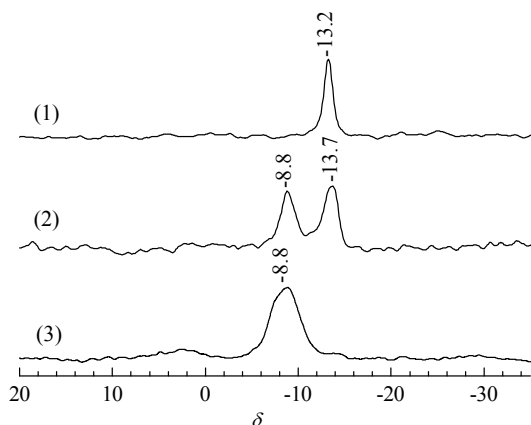


Fig. 1.  $^{31}P$  MAS NMR spectra of  $Q^{18}P_2W_{18}$  (1),  $Q^{18}P_2W_{17}$  (2), and  $Q^{18}P_2W_{12}$  (3).

Obviously, the structures of the heteropolyanions  $[P_2W_{18}O_{62}]^{6-}$  and  $[P_2W_{17}O_{61}]^{10-}$  show no changes during the synthesis of  $Q^{18}P_2W_{18}$  and  $Q^{18}P_2W_{17}$  by their assembly with the quaternary ammonium cations. However, the peak at  $\delta = -8.8$  for  $Q^{18}P_2W_{12}$  is very broad and asymmetric as it has a small shoulder peak, which indicates that the structures of the heteropolyanion  $[\alpha-H_2P_2W_{12}O_{48}]^{12-}$  is distinctly distorted in the  $^{31}P$  MAS NMR spectrum of  $Q^{18}P_2W_{12}$ , but the original structure remained intact.

Figure 2 shows FT-IR spectra of  $Q^{18}P_2W_{18}$ ,  $Q^{18}P_2W_{17}$ , and  $Q^{18}P_2W_{12}$ . The P=O bands at ca. 1090  $cm^{-1}$  for  $Q^{18}P_2W_{18}$ , ca. 1086  $cm^{-1}$  for  $Q^{18}P_2W_{17}$ , and 1140 and 1086  $cm^{-1}$  for  $Q^{18}P_2W_{12}$  further indicate the retention of the basic Dawson framework compared with their corresponding potassium salts. Moreover, the bands at ca. 1468  $cm^{-1}$  are due to a contribution from the deformation vibrations of the C–H that belongs to  $CH_3$  or  $CH_2$ . The asymmetric stretching vibrations of C–H are found at ca. 2921  $cm^{-1}$  and the symmetric stretching vibrations of C–H are at ca. 2851  $cm^{-1}$ , which results from the  $CH_3$  or  $CH_2$  in the octadecyltrimethylammonium cations. Therefore, quaternary ammonium cations and polytungstophosphates anions efficiently combine with each other by electrostatic interactions.

It has been found that  $K_{12}[\alpha-H_2P_2W_{12}O_{48}]$ , which is insoluble in model oil, has no activity during BT oxidation under the present conditions. The reaction mixture is a two-liquid phase system, and mass transfer affects the reaction negatively. However, the conversion of BT is greatly increased upon catalysis by  $Q^{18}P_2W_{12}$ , with 62% conversion at 30 °C for 1 h. The reason is that the  $Q^{18}P_2W_{12}$  that was synthesized in a moderate acidic solution by an organic combination between quaternary ammonium cations and polytungstophosphates can improve the formation of an emulsion and the reaction efficiency between BT and  $H_2O_2$ .

The activity of  $Q^{18}P_2W_{18}$ ,  $Q^{18}P_2W_{17}$ , and  $Q^{18}P_2W_{12}$  during

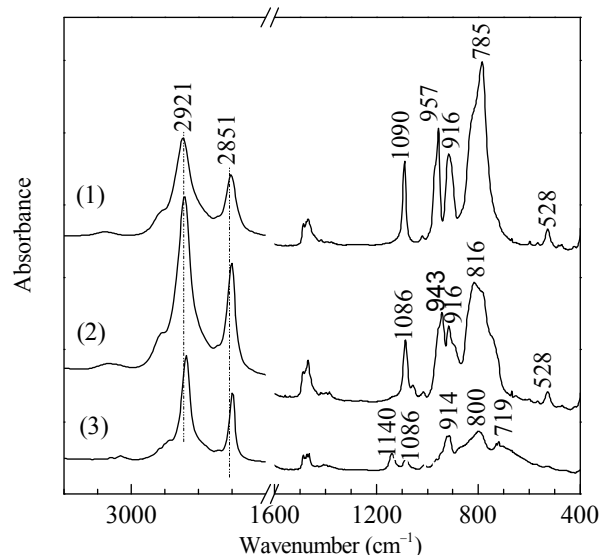
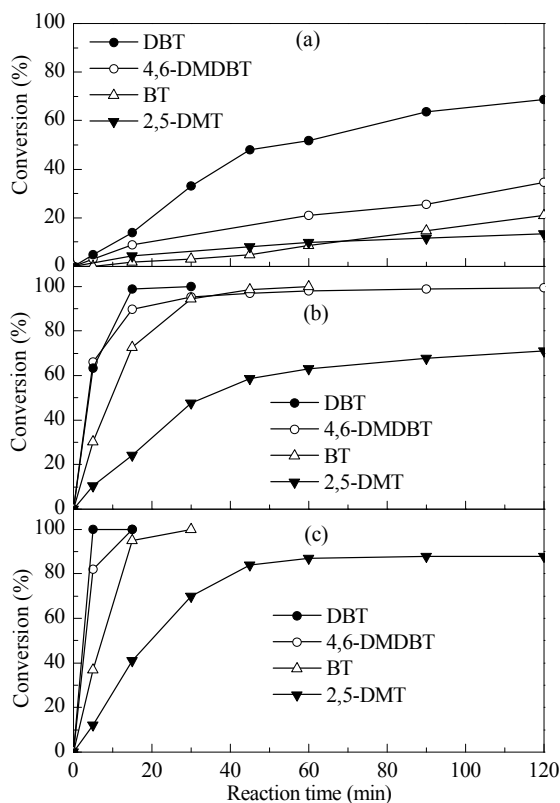


Fig. 2. FT-IR spectra of  $Q^{18}P_2W_{18}$  (1),  $Q^{18}P_2W_{17}$  (2), and  $Q^{18}P_2W_{12}$  (3) samples.



**Fig. 3.** The conversion of the different sulfur-containing compounds catalyzed by  $Q^{18}P_2W_{18}$  (a),  $Q^{18}P_2W_{17}$  (b), and  $Q^{18}P_2W_{12}$  (c). Reaction conditions: Model oil (S in decalin = 1000 ng/ $\mu$ l) 12.5 ml, catalyst 30 mg,  $H_2O_2/S = 3$ , 60 °C.

the oxidation of 4,6-DMDBT, DBT, BT, and 2,5-DMT was investigated under mild conditions (Fig. 3). At 60 °C, the conversion of DBT was 100% within 5 h, 30 min, and 5 min when catalyzed by  $Q^{18}P_2W_{18}$ ,  $Q^{18}P_2W_{17}$ , and  $Q^{18}P_2W_{12}$ , respectively. As shown in Fig. 3, the activities of  $Q^{18}P_2W_{12}$  and  $Q^{18}P_2W_{17}$  are much higher than that of  $Q^{18}P_2W_{18}$ , which could be related to the formation of active polyperoxometalate in the  $H_2O_2$ -based reaction system.  $Q^{18}P_2W_{12}$  and  $Q^{18}P_2W_{17}$ , which are both lacunary Dawson-type heteropolycompounds, can be more easily transformed into active polyperoxometalates in the presence of hydrogen peroxide according to the published work [16]. Moreover,  $Q^{18}P_2W_{12}$  is much more unstable than  $Q^{18}P_2W_{17}$  [17] and can be much more easily transformed into an active polyperoxometalate. Therefore,  $Q^{18}P_2W_{12}$  has the best activity for BT oxidation among the three studied catalysts and their activity decreases in the order:  $Q^{18}P_2W_{12} > Q^{18}P_2W_{17} > Q^{18}P_2W_{18}$ . The oxidative reactivity order of the sulfur-containing compounds is  $DBT > 4,6-DMDBT > BT > 2,5-DMT$ .

The oxidative reactivity order of the sulfur-containing compounds is basically related to the electron density of the sulfur atom in sulfur-containing compounds [20]. However, steric hindrance because of methyl substitution in 4,6-DMDBT hinders the interaction between 4,6-DMDBT and the catalyst.

Therefore, the reaction rate of DBT oxidation is higher than that of 4,6-DMDBT although the electron density at the sulfur atom of DBT is lower than that of 4,6-DMDBT.

In summary, Dawson-type polyoxotungstate emulsion catalysts could efficiently catalyze the oxidation of sulfur-containing compounds to their corresponding sulfones under mild conditions.  $Q^{18}P_2W_{12}$  has a very high activity for the oxidation of sulfur-containing compounds.

## Acknowledgments

The authors would like to thank Prof. YANG Qihua for correcting expressions in the manuscript and making several helpful suggestions.

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