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用 Dawson 型聚氧钨酸乳液催化氧化燃油超深度脱硫

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摘要: 合成了 Dawson 型聚氧钨酸乳液催化剂 $Q^{18}P_2W_{18}$, $Q^{18}P_2W_{17}$, 和 $Q^{18}P_2W_{12}$. 采用红外光谱和固体核磁技术对其进行了表征, 并用于温和条件下 H_2O_2 氧化 4,6-二甲基二苯并噻吩 (4,6-DMDBT)、二苯并噻吩 (DBT)、苯并噻吩 (BT) 和 2,5-二甲基噻吩 (2,5-DMT) 等含硫化合物的反应中. 结果表明, 各催化剂的活性大小顺序为 $Q^{18}P_2W_{12} > Q^{18}P_2W_{17} > Q^{18}P_2W_{18}$. 含硫化合物的氧化活性顺序为 DBT > 4,6-DMDBT > BT > 2,5-DMT. 在 60 °C 反应 30 min 内, $Q^{18}P_2W_{12}$ 催化剂能够催化氧化 BT 完全转化成相应的砜.

关键词: Dawson 型; 聚氧钨酸盐; 乳液催化剂; 氧化脱硫
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Ultra-deep Oxidative Desulfurization of Fuel Oil Catalyzed by Dawson-Type Polyoxotungstate Emulsion Catalysts

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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-dimethythiophene (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

随着环境法规越来越严格, 燃油脱硫已成为世界范围内急需解决的重要课题之一. 在石油炼制工业中, 加氢脱硫 (HDS) 是一种传统的脱硫方法[1~3]. 但对于位阻较大的 4,6-二甲基二苯并噻吩 (4,6-DMDBT) 及其衍生物则比较难以脱除. 因此, 为了实现超深度脱硫, 必须用更高的温度和压力、甚至活性更高的催化剂等苛刻条件, 这势必增加操作成本. 氧化脱硫 (ODS) 操作条件温和且不耗氢, 因而认为是一种非常有前途的脱硫替代技术之一[4]. 在 ODS 过程中, 燃油中含硫化合物先被氧化成砜, 后者可用极性溶剂萃取除去[5].

用于 ODS 的催化剂较多, 如钛硅分子筛[6~8]、金属氧化物[9]以及聚氧多金属酸盐[10~13]等. 李灿课题组曾采用几种乳液催化剂磷钨杂多酸季铵盐用于燃油中含硫化合物的氧化[14~16], 且不需要另加腐蚀性有机酸、极性萃取剂和极性溶剂. 另外, 这种催化剂可使反应体系乳化, 从而促进含硫化合物和 H_2O_2 之间的反应. 在这种乳液体系中, 具有 Keggin 结构的

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缺陷型聚氧钨酸盐催化剂对含硫化合物氧化具有较高的催化活性[16]. 但是, 有关 Dawson 型杂多化合物在氧化脱硫方面的研究未见报道. 因此, 本文合成了 Dawson 型杂多酸乳液催化剂, 并研究了其对含硫化合物的催化氧化性能.

首先, 根据文献[17]分别制备杂多酸钾盐 $K_6[P_2W_{18}O_{62}]\cdot 14H_2O$、$K_{10}[P_2W_{17}O_{61}]\cdot 20H_2O$ 和 $K_{12}[\alpha\text{-}H_2P_2W_{12}O_{48}]\cdot 24H_2O$. 分别将 0.21~0.22 mmol 上述钾盐溶解在 15~30 ml 去离子水中, 适当用 4 mol/L 的 HCl 溶液调节溶液酸性, 再逐滴加入含有 2.1~2.2 mmol 十八烷基三甲基氯化铵 (CTAC) 的乙醇溶液, 立即生成浅蓝色或者白色沉淀. 搅拌 1 h 后, 过滤, 于 60 °C 真空烘干, 分别得到相应的催化剂, 记为 $Q^{18}P_2W_{18}$, $Q^{18}P_2W_{17}$ 和 $Q^{18}P_2W_{12}$.

^{31}P 核磁共振实验在 Bruker DRX-400 型核磁共振波谱仪上进行, BBO MAS 探头和 4 mm ZrO_2 旋转头, 共振频率 161.8 MHz, 采用高强度质子去偶, 脉冲宽度 2.0 μs, 重复时间 2 s, 2048 次扫描, 旋转频率 10 kHz. 化学位移以 85%H_3PO_4 水溶液为参比. 傅里叶红外 (FT-IR) 表征在 Nicolet 470 型红外光谱仪上进行, 样品采用 KBr 压片.

氧化反应过程如下. 在 60 °C 将 0.39 mmol 含硫化合物 2,5-二甲基噻吩 (2,5-DMT)、苯并噻吩 (BT)、二苯并噻吩 (DBT) 或 4,6-DMDBT 溶于 12.5 ml 十氢萘中, 配制成硫含量为 1000 ng/μl 的模型油. 在 1000 r/min 转速搅拌下, 0.0044 mmol 催化剂和 0.14 ml 30% H_2O_2 分别快速加到模型油中, 可以观察到形成浑浊乳状液. 随着反应的进行, 每小时取样并冷藏使反应停止, 离心后催化剂和液相分离. 用配备火焰光度检测器 (FPD, Agilent H9261 型) 的气相色谱仪 (GC, Agilent 6890N 型, 色谱柱为 PONA, 50 m × 0.2 mm × 0.5 μm) 分析所取样品中油相的含硫量.

图 1 为各催化剂的 ^{31}P MAS NMR 谱. 由图可见, $Q^{18}P_2W_{18}$ 样品于 $\delta = -13.2$ 出现谱峰; $Q^{18}P_2W_{17}$ 于 $\delta = -8.8$ 和 -13.7 处出现双谱峰; 而 $Q^{18}P_2W_{12}$ 仅在 $\delta = -8.8$ 出现单谱峰, 与文献结果一致[17~19]. 可见, $Q^{18}P_2W_{18}$ 和 $Q^{18}P_2W_{17}$ 仍保持 Dawson 型杂多阴离子 $[P_2W_{18}O_{62}]^{6-}$ 和 $[P_2W_{17}O_{61}]^{10-}$. 但 $Q^{18}P_2W_{12}$ 谱峰非常宽, 且因明显的弱小肩峰存在而不对称, 而类似磷物种出现在此化学位移内尚未见报道, 这说明催化剂 $Q^{18}P_2W_{12}$ 中杂多阴离子 $[\alpha\text{-}H_2P_2W_{12}O_{48}]^{12-}$ 的结构发生明显扭曲, 但是依然保持其完整的原始结构.

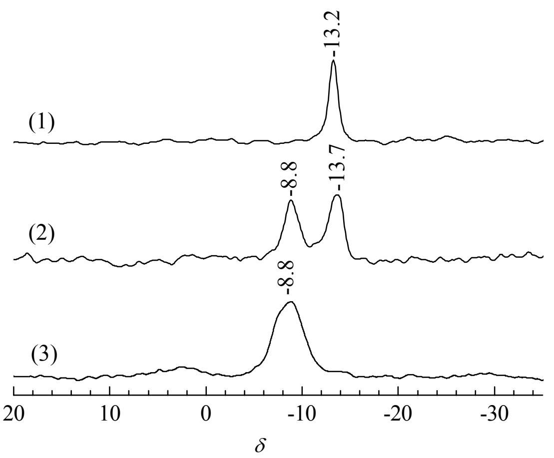

图 1 $Q^{18}P_2W_{18}$, $Q^{18}P_2W_{17}$ 和 $Q^{18}P_2W_{12}$ 的 ^{31}P MAS NMR 谱

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).

图 2 为 $Q^{18}P_2W_{18}$, $Q^{18}P_2W_{17}$ 和 $Q^{18}P_2W_{12}$ 样品的 FT-IR 谱. 由图可见, $Q^{18}P_2W_{18}$, $Q^{18}P_2W_{17}$ 和 $Q^{18}P_2W_{12}$ 样品分别在 1090, 1086 以及 1140 和 1086 cm^{-1} 处出现归属于 P=O 的不对称伸缩振动峰. 这说明样品均完整保持了相应的 Dawson 型骨架结构. 另外, 还可以观察到 CH_3 和 CH_2 基团的 C–H 弯曲振动 (1468 cm^{-1}) 及其不对称 (2921 cm^{-1}) 和对称伸缩振动 (2851 cm^{-1}). 这些都源于十八烷基三甲基季铵盐阳离子中 CH_3 和 CH_2 基团. 同时也说明季铵盐阳离子和多聚磷钨酸阴离子通过静电作用而进行了有效地结合.

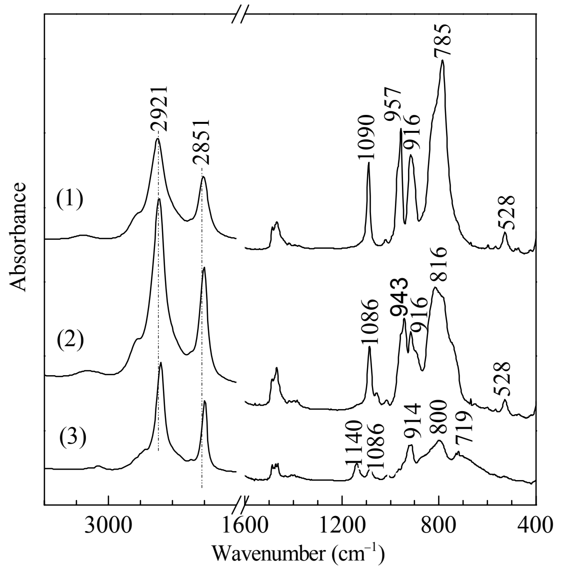

图 2 $Q^{18}P_2W_{18}$, $Q^{18}P_2W_{17}$ 和 $Q^{18}P_2W_{12}$ 样品的 FT-IR 谱.

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.

实验证实，在本文所采用的实验条件下，$K_{12}[\alpha\text{-}H_2P_2W_{12}O_{48}]$对BT氧化没有明显的催化活性. 这是因为这种钾盐不溶于模型油, 整个反应体系是一个水油不互溶的两相体系, 含硫化合物、氧化剂和催化剂之间不能有效地接触, 因而严重阻碍了催化剂发挥其催化作用. 但是在$Q^{18}P_2W_{12}$的催化作用下, BT转化率明显提高, 即便在30 °C, 1 h内BT转化率也达62%. 这是由于在温和的酸性条件下, 季铵盐和多聚磷钨酸盐有机的结合促进了乳液的形成, 有利于BT和H_2O_2之间的反应.

图3为$Q^{18}P_2W_{18}$, $Q^{18}P_2W_{17}$和$Q^{18}P_2W_{12}$催化剂上4,6-DMDBT, DBT, BT和2,5-DMT氧化反应活性. 由图可见，在60 °C时，$Q^{18}P_2W_{18}$, $Q^{18}P_2W_{17}$和$Q^{18}P_2W_{12}$催化DBT完全转化所需时间分别为5 h, 30 min和5 min. 可见, $Q^{18}P_2W_{12}$和$Q^{18}P_2W_{17}$活性要比$Q^{18}P_2W_{18}$高很多. 这可能与杂多阴离子在H_2O_2中极易向活性的多聚过氧化物转化有关. 与文献[16]类似, $Q^{18}P_2W_{12}$和$Q^{18}P_2W_{17}$都是缺陷型Dawson杂多化合物, 在H_2O_2存在下, 比较易于转化生成活性多聚过氧化物. 而且, $Q^{18}P_2W_{12}$稳定性不及$Q^{18}P_2W_{17}$[17], 向活性多聚过氧化物转化的速度更快. 因此, $Q^{18}P_2W_{12}$在BT等含硫化合物氧化反应中活性最高, 各催化剂活性依序递减: $Q^{18}P_2W_{12} > Q^{18}P_2W_{17} > Q^{18}P_2W_{18}$. 还可以发现, 在各催化剂催化作用下, 含硫化合物反应活性依序递减: DBT > 4,6-DMDBT > BT > 2,5-DMT.

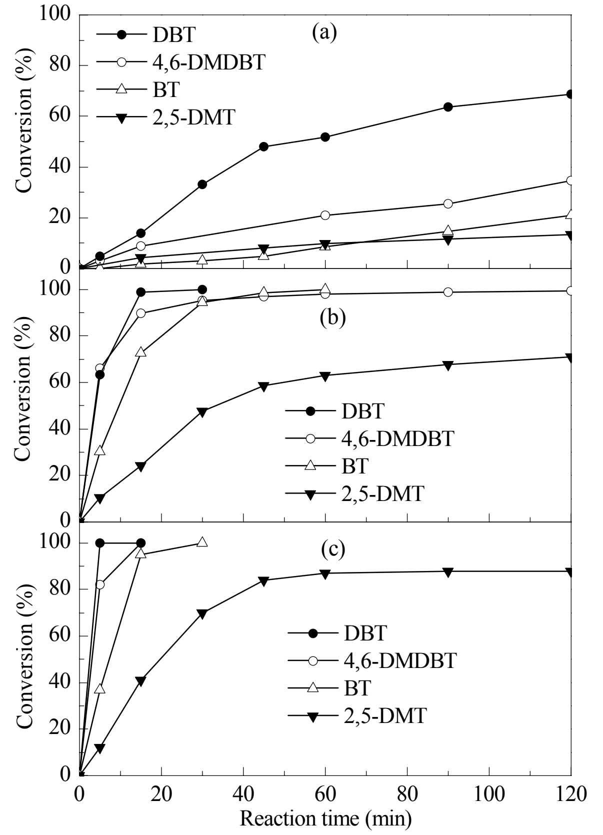

图3 $Q^{18}P_2W_{18}$, $Q^{18}P_2W_{17}$和$Q^{18}P_2W_{12}$催化剂对不同含硫化合物的催化氧化活性

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/μl) 12.5 ml, catalyst 30 mg, $H_2O_2/S = 3$, 60 °C.

含硫化合物的氧化反应性高低与其S原子的电子云密度高低趋势一致[20]. 但是, 由于4,6-DMDBT分子侧位甲基位阻效应较大, 以至于影响它和催化剂间相互作用. 因此, 尽管DBT中S原子电子云密度低于4,6-DMDBT, 但其氧化反应速率却比4,6-DMDBT更大.

总而言之, 在温和条件下, Dawson型聚氧钨酸乳液催化剂能够有效地将含硫化合物氧化成相应的砜, 其中以$Q^{18}P_2W_{12}$催化剂活性最高.

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英 译 文

English Text

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 $K_{12}[\alpha\text{-}H_2P_2W_{12}O_{48}]\cdot 24H_2O$ 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), respectively. 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 μs 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-Dimethythiophene (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/μl. 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 × 0.2 mm × 0.5 μm).

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]. 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 $[\alpha\text{-}H_2P_2W_{12}O_{48}]^{12-}$ 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 $K_{12}[\alpha\text{-}H_2P_2W_{12}O_{48}]$, which is unsoluble 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 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.

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