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COMMUNICATION

Oxidation of refractory sulfur-containing compounds with molecular oxygen catalyzed by vanadoperiodate

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A new vanadoperiodate $[HIV_9O_{28}]^{3-}$ has been synthesized by a simple, one-pot stoichiometric reaction of $HIO_4 \cdot 2H_2O$ with $NaVO_3$ in aqueous solution, and then isolated as $[C_8H_{17}N(CH_3)_3]_3HIV_9O_{28}$ by cation exchange. We found that $[C_8H_{17}N(CH_3)_3]_3HIV_9O_{28}$ shows high catalytic activity in oxidation of refractory sulfur-containing compounds to their corresponding sulfones using molecular oxygen as oxidant under mild reaction conditions.

Oxidation of sulfur-containing compounds with molecular oxygen is not only an interesting subject of organic chemistry, but also a challenging goal for clean fuel production. One of the promising strategies to remove the sulfur-containing compounds from fuels (e.g. diesel) is the oxidative desulfurization (namely, the oxidation of sulfur-containing compounds and then followed an absorption or extraction process to remove the sulfones from fuels; ODS for short). The ODS avoids the use of expensive hydrogen and allows the process to be conducted under mild conditions. Most importantly, the ODS can show high efficiency in removing refractory compounds, predominantly 4,6-dimethylbenzothiophenes (4,6-DMDBT) with oxidants such as organic and inorganic peroxy acids, hydrogen peroxide (H_2O_2), peroxy salts, NO_2, *tert*-butyl-hydroperoxide, ozone (O_3), *etc.*[1-5] Molecular oxygen is a green and abundantly available cheap oxidant. The utilization of molecular oxygen as oxidant for ODS without adding additional reagents is highly desirable, but very challenging because the activation of molecular oxygen is difficult under mild conditions.[6, 7]

Polyoxometalates (POMs) are attractive compounds and their molecular properties (composition, size, shape, charge density, thermal stability and redox potential) can be tuned in a wide range. [8-10] Because of their resistance toward oxidation and compatibility with various oxygen source, POMs are potentially the oxidation catalysts.[11-14] Polyoxovanadates (POVs) as a new subclass of POMs has received increasing attention. [9, 15, 16]

In this work, for the first time we found that the vanadoperiodate $[C_8H_{17}N(CH_3)_3]_3HIV_9O_{28}$ ($(Q_8)_3HIV_9O_{28}$ for short) shows high catalytic activity in oxidizing dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (4,6-DMDBT) to their corresponding sulfones using molecular oxygen as oxidant under mild reaction conditions. The ESR and Uv-vis spectra results indicate that the molecular oxygen is activated via a superoxo-like intermediate coordinated with the vanadoperiodate in the oxidation process.

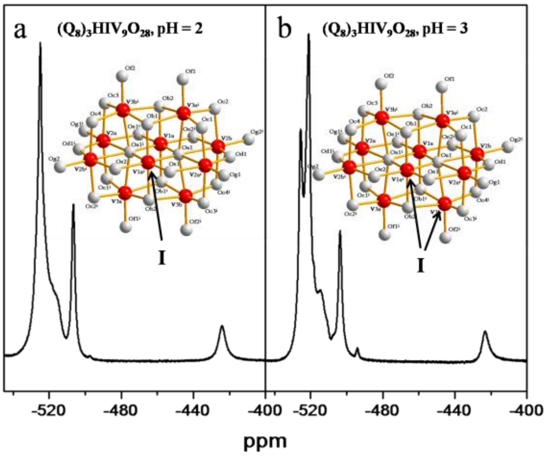


Fig. 1 ^{51}V NMR spectra of vanadoperiodate polyanion with different pH value put in the formula of the polyanion . (a) pH = 2; (b) pH = 3.

The polyanion $[HIV_9O_{28}]^{3-}$ was synthesized by a simple, one-pot stoichiometric reaction of $HIO_4 \cdot 2H_2O$ with $NaVO_3$ in aqueous solution, and then isolated as $(Q_8)_3HIV_9O_{28}$ by cation exchange. The IR spectrum of $(Q_8)_3HIV_9O_{28}$ is similar to that of decavanadate (see Fig. S1). The very strong band at 977 cm^{-1} is assigned to the stretching of terminal V-O bond. The strong bands that appear at higher frequencies between 860 and 610 cm^{-1} are corresponding to the asymmetrical $V-O_b-V$ stretching vibrations. The weak bands between 551 and 400 cm^{-1} are corresponding to the symmetrical $V-O_b-V$ stretching vibrations.[17-19] The band at 910 cm^{-1} is attributed to the stretching of $I-O_b-V$ bond. Fig. 1 shows the ^{51}V NMR spectrum of vanadoperiodate polyanion at different pH value. The ^{51}V NMR spectra of $[HIV_9O_{28}]^{3-}$ exhibit only 3 broad peaks, which are similar to that of decavanadate (Fig. 1a, Fig. S2). The peaks at -524, -506 and -424 ppm are attributed to capping, corner and central V atom. Replacement with I atom at central V atom has the same influence on all the corner and capping V atom, and the relative peak intensity between corner and capping V atom does not change. Whereas, replacement with I atom at capping V atom leads to the difference of the relative peak intensity between corner and capping V atom. The two replacements lead to different chemical environment of corner V atoms. These results

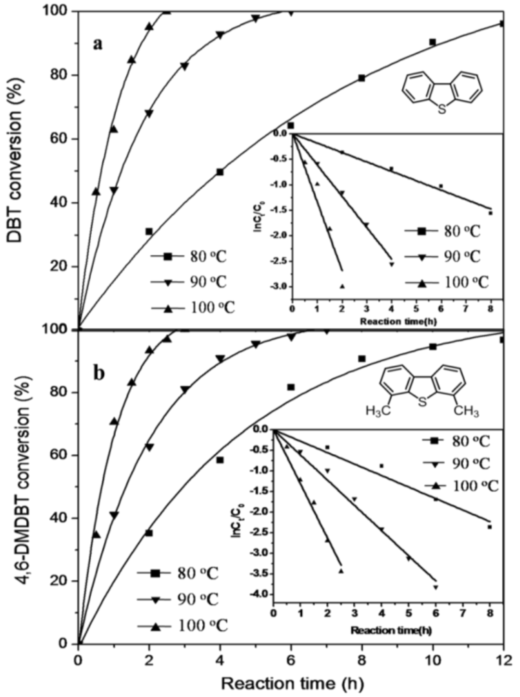


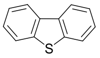
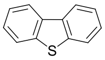
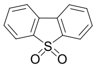
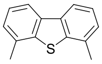
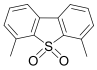
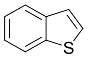
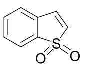
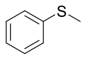
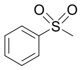
Fig. 2 (a) The conversion of DBT and ln(C_t/C_0) *vs*. reaction time at different temperatures. (b) The conversion of 4,6-DMDBT and ln(C_t/C_0) *vs*. reaction time at different temperatures. Reaction conditions: $(Q_8)_3HIV_9O_{28}$ (40 mg), DBT, 4,6-DMDBT (S: 500 ppm) in 20 ml decalin, oxidant O_2 (1 atm).

indicate that replacement with I atom (pH = 2) takes place only at central V atom and replacement with I atom (pH = 3) takes place at both central and capping V atom of decavanadate. In this work we use the vanadoperiodate with only central V atom replaced given the formula of the vanadoperiodate.

Oxidation of DBT was conducted in a flask with O_2 gas bubbled at 90 ºC, and the products were analyzed at different reaction times. The products were analyzed with sulfur-specific gas chromatography (GC) before and after the catalytic oxidation of DBT in decalin (see Fig. S3). A white needle-type crystal was obtained when reaction system was cooled down to room temperature. The products were determined to be the crystallized dibenzothiophene sulfone ($DBTO_2$), characterized by IR (see Fig. S4) and ^1H NMR (δ (ppm): 8.20 (2 H), 7.98 (2 H), 7.80 (2 H), 7.65 (2 H)) (see Fig. S5). The mass spectrum of product shows the molecular ion peak at 216 *m/z*, which is in good agreed with the molecular weight of $DBTO_2$.[22]

A series of oxidation reactions were carried out to investigate the effect of temperature on the conversion efficiency of DBT and 4,6-DMDBT (see Fig. 2). Enhancing temperature from 80 to 100 ºC led to a remarkable increase of the conversion of DBT and 4,6-DMDBT. The C_t/C_0 was defined as the ratio of the concentration of final and initial sulfur-containing compounds. The linear fit of ln(C_t/C_0) against the reaction time demonstrates the pseudo-first-order kinetics characteristics for the oxidation of DBT and 4,6-DMDBT on $(Q_8)_3HIV_9O_{28}$. Table 1 gives the oxidation of general typical sulfur-containing compounds most possibly present in oil on the $(Q_8)_3HIV_9O_{28}$ using molecular oxygen as oxidant. The result indicates that activity on oxidation of sulfur-containing compounds increases with the increase of electron density. [23]

Table 1. Oxidation of sulfur compound by molecular oxygen.[a]

Catalyst	Sulfur compound	Product	Time /h	electron density	yield (%)
No catalyst		N.D.[b]	12	5.758	0
$(Q_8)_3HIV_9O_{28}$			6	5.758	100
$(Q_8)_3HIV_9O_{28}$			7	5.760	100
$(Q_8)_3HIV_9O_{28}$			12	5.739	63
$(Q_8)_3HIV_9O_{28}$			4	5.915	98

[a] Reaction conditions: $(Q_8)_3HIV_9O_{28}$ (40 mg), Sulfur containing compounds in decalin (0.3 mmol), reaction temperature 90 ºC and O_2 (1 atm). [b] Not detected.

Catalyst can be isolated by centrifugation after oxidation since catalyst was insoluble in decalin, and washed by entanol. It is notable that the recovered catalyst could be reused for the oxidation of DBT keeping the high catalytic performance; 99% conversion of DBT for the first run, 98% for the second run, and 99% for the third run.

To investigate the details of the aerobic oxidation of sulfur-containing compounds, a series of experiments were designed. Experiment 1: Argon was bubbled into 20 ml decalin for 30 min to expel dissolved oxygen at 90 ºC. 40 mg $(Q_8)_3HIV_9O_{28}$ and 0.3 mmol DBT were added into decalin in argon atmosphere under vigorously stirring for 4 hours. Experiment 2: 20 ml decalin and 40 mg $(Q_8)_3HIV_9O_{28}$ were added into a flask with molecular oxygen bubbled for 2 hours under vigorously stirring at 90 ºC. And then, argon was bubbled for 30 min to expel residual oxygen. 0.3 mmol DBT was added and reacted for 4 hours. GC-FPD results shows only one peak (see Fig. S6) corresponding to DBT (retention time: 4.2 min) in the sample of experiment 1. Whereas, both peaks corresponding to DBT and $DBTO_2$ can be observed in experiment 2. These results indicate that DBT is oxidized by

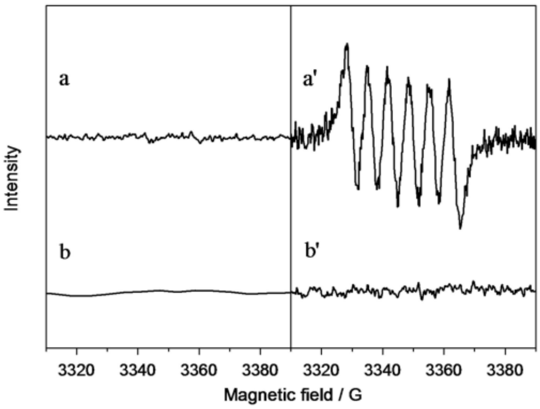


Fig. 3 *In situ* ESR spectra of DMPO-$O_2^{\cdot-}$ adduct generated in the oxidative desulfurization process. (a) the sample tested without catalyst at 60 ºC. (b) the sample tested without catalyst at 25 ºC. (a') the sample tested with catalyst at 60 ºC. (b') the sample tested with catalyst at 25 ºC.

an active intermediate, which is generated via the reaction of molecular oxygen with $(Q_8)_3HIV_9O_{28}$.

To study the interaction of $(Q_8)_3HIV_9O_{28}$ with molecular oxygen, ESR spin-trap technique with DMPO as a trap for $O_2^{\cdot -}$ was employed. Fig. 3 shows the ESR signals obtained from *in situ* oxidation of DBT process. No ESR signals were observed at 25 °C and 60 °C for the reaction system without $(Q_8)_3HIV_9O_{28}$. With introduction of $(Q_8)_3HIV_9O_{28}$ no ESR signal was observed at 25 °C either. When the reaction system was heated to 60 °C, a broad, 6-line ESR signal appeared. The hyperfine splittings are α_N = 13.6 G and α_H^{β} = 7.2 G. The sextet ESR signals can be assigned to DMPO-$O_2^{\cdot -}$ adduct.[7, 24-27] We also found that the ESR signal intensity is increased with temperature increasing (see Fig. S7). These results indicate that $O_2^{\cdot -}$ is produced through the reaction of $(Q_8)_3HIV_9O_{28}$ with molecular oxygen.

To further understand the coordination and activation of O_2 in the catalyst, UV-Vis spectrum of reaction system was measured. An absorption band at 226 nm is observed when $(Q_8)_3HIV_9O_{28}$ is dissolved in decalin under argon at 90 °C (Fig. 4). The band at 226 nm can be attributed to a ligand-to-metal charge-transfer (LMCT) transition. With introduction of O_2, the absorption band shows a blue shift to 218 nm. The band at 218 nm has been attributed to the superoxo to vanadium LMCT transition ($\pi v^* \rightarrow d\sigma^*$).[28, 29] It appears that vanadium-superoxo complexes were formed through the coordination of superoxo to the vanadium complex. Similar absorption bands exhibit with and without addition of DBT (see Fig. S8). This result also suggests that DBT is not oxidized by $(Q_8)_3HIV_9O_{28}$ alone. Therefore, we proposed a plausible mechanism. First, the molecular oxygen is activated in the form of vanadium-superoxo complexes when molecular oxygen coordinates to $(Q_8)_3HIV_9O_{28}$. Then, the vanadium-superoxo complexes oxidized DBT to $DBTO_2$.

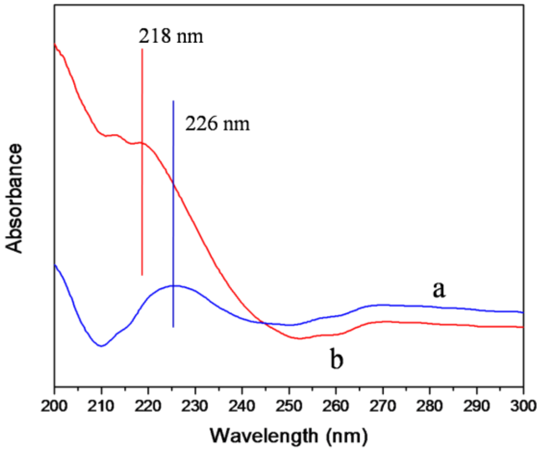


Fig. 4 UV-vis spectra of $(Q_8)_3HIV_9O_{28}$. All spectra were collected from 30 mg L^{-1} solution. (a) $(Q_8)_3HIV_9O_{28}$ dissolved in decalin at 90 °C for 1 h under 1 atm Ar; (b) $(Q_8)_3HIV_9O_{28}$ dissolved in decalin after treatment with 1 atm O_2 at 90 °C for 1 h.

In summary, we have synthesized a monoiodine(VII) derivative of the decavanadate. The vanadoperiodate shows high catalytic activity in the oxidation of dibenzothiophene and its derivatives to their corresponding sulfones using molecular oxygen. Molecular oxygen is activated through the formation of vanadium-superoxo species. This work discovered a new catalyst $(Q_8)_3HIV_9O_{28}$, which can activate the molecular oxygen and catalyze the oxidation of sulfur-containing molecules into sulfones.

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Notes and references

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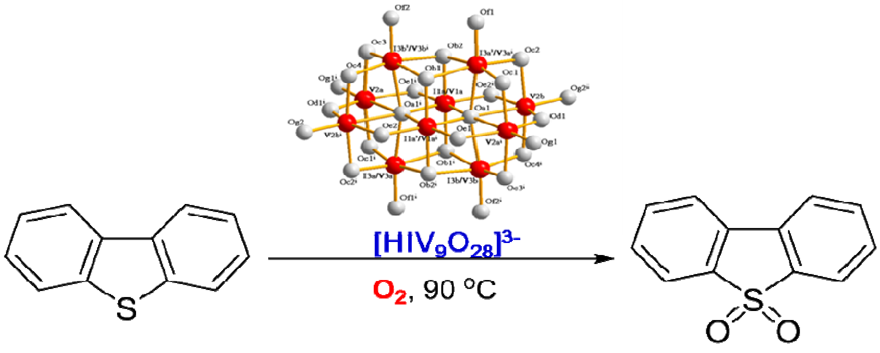
Graphical Abstract



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