ChemComm

COMMUNICATION

Oxidation of dibenzothiophene catalyzed by $[C_8H_{17}N(CH_3)_3]_3H_3V_{10}O_{28}$ using molecular oxygen as oxidant†

Nanfang Tang,[a] **Yongna Zhang,**[a] **Feng Lin,**[a] **Hongying Lü,**[a] **Zongxuan Jiang***[a] **and Can Li***[a]

An isopolyoxovanadate catalyst $[C_8H_{17}N(CH_3)_3]_3H_3V_{10}O_{28}$ shows high catalytic activity in oxidation of dibenzothiophene (DBT) to its corresponding sulfone using molecular oxygen as oxidant under mild reaction conditions. This is potentially a promising approach to achieve ultradeep desulfurization of fuels (*e.g.* diesel) because the sulfones can be more conveniently removed from the fuels by either extraction or selective adsorption.

Sulfur compounds are undesirable in fuels, which are the major source of air pollution. The Environmental Protection Agency (EPA) regulations and EU Euro V standards called for the sulfur level in diesel fuel to be less than 15 and 10 ppmw S, respectively. Hydrodesulfurization is highly efficient for the removal of thiols, sulfides and disulfides. However, it is difficult to reduce refractory sulfur-containing compounds such as dibenzothiophene (DBT) and its derivatives especially 4,6-dimethyldibenzothiophene (4,6-DMDBT) to an ultra low level using only conventional HDS. Severe operating conditions such as high temperatures, high pressures, and high hydrogen consumption are required for HDS to achieve the ultra-deep desulfurization of diesel. High capital and operating costs are inevitable. Therefore, it is absolutely necessary to develop new approaches for ultra-deep desulfurization of fuels.[1–5] Oxidative desulfurization (ODS) as one of the most promising alternative technologies has attracted much attention.[6,7] The ODS avoids the use of hydrogen and allows the process to be conducted under ambient conditions. Moreover, refractory compounds, predominantly 4,6-DMDBT, could be removed efficiently, which however are difficult to remove through conventional HDS.

Many types of oxidative systems have been investigated for oxidative desulfurization, such as H_2O_2–polyoxometalate,[8] H_2O_2–formic-acid,[9–11] H_2O_2–ionic liquids,[12] H_2O_2–emulsion catalysts,[13–15] H_2O_2–iron-complexes,[16] H_2O_2–acetic-acid,[17] H_2O_2–solid bases,[18] H_2O_2–TiSi,[19] and other non-hydrogen peroxide systems (*e.g.*, *t*-butyl hydroperoxide, NO_2, *etc.*).[20,21] Those catalytic ODS processes based on H_2O_2 show high efficiency,

but have disadvantages such as thermal instability (H_2O_2). Taking account of environmental, safety, and economic concerns, the utilization of O_2 as the oxidant for ODS is most desirable.

In this communication, we report a highly-efficient and highly-selective oxidative desulfurization of dibenzothiophene (DBT) using molecular oxygen catalyzed by isopolyoxovanadate $[C_8H_{17}N(CH_3)_3]_3H_3V_{10}O_{28}$ ($Q_3H_3V_{10}O_{28}$ for short) under mild conditions.‡ Oxidation of DBT-containing model oil was conducted in a flask with O_2 gas bubbled at 90 °C, and the products were analyzed at different reaction times. Fig. 1 shows the sulfur-specific gas chromatography (GC) analyses before and after the catalytic oxidation of DBT in decalin. With increasing reaction time, it is clear that the peak area for DBT decreases, whereas the peak area corresponding to dibenzothiophene sulfone ($DBTO_2$) (retention time: 5.9 min) increases. No DBT was observed in the treated fuel after 7 h of reaction, indicating that all of DBT has been converted into $DBTO_2$. We could obtain white needle-type crystals when the reaction system was cooled to room temperature, which are $DBTO_2$ (confirmed by the IR spectrum, see Fig. S1, ESI†). According to the above experiments, we can come to a conclusion that the DBT
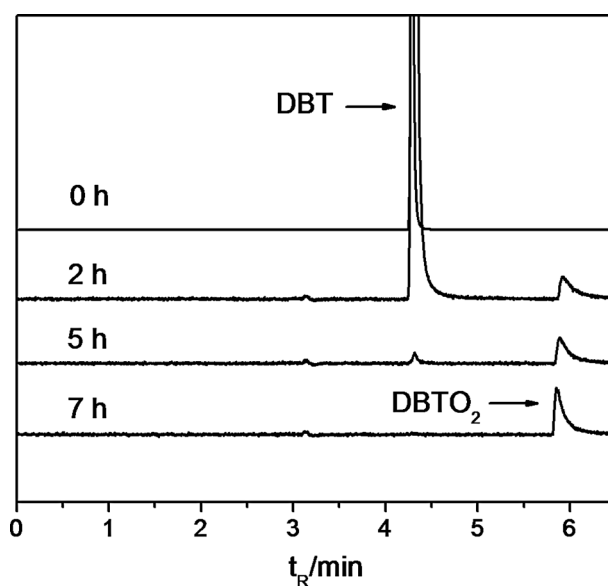
[a] *State Key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Chinese Academy of Sciences, Dalian 116023, China. E-mail: zxjiang@dicp.ac.cn, canli@dicp.ac.cn*
[b] *Graduate School of Chinese Academy of Sciences, Beijing 100049, China*

Fig. 1 Sulfur-specific GC-FPD chromatograms of the oxidation of DBT in decalin. Reaction conditions: $Q_3H_3V_{10}O_{28}$ (40 mg), DBT (S: 500 ppm) in 20 mL decalin, reaction temperature 90 °C, oxidant O_2 (1 atm).

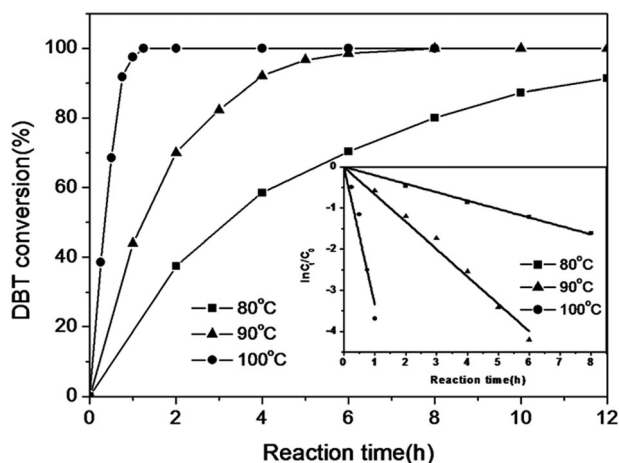**Fig. 2** The conversion of DBT *vs.* reaction temperature. Reaction conditions: $Q_3H_3V_{10}O_{28}$ (40 mg), DBT (S: 500 ppm) in 20 mL decalin, oxidant O_2 (1 atm).

present in decalin can be oxidized into $DBTO_2$ catalyzed by $Q_3H_3V_{10}O_{28}$ using molecular oxygen as oxidant.

Fig. 2 shows the removal of DBT and $\ln(C_t/C_0)$ *vs.* reaction time, which reveals the catalytic reaction kinetics. Increasing reaction temperature from 80 to 100 °C leads to a remarkable increment of the conversion of DBT. At 100 °C, the conversion of DBT was up to 100% in 1.25 h. The linear fit of $\ln(C_t/C_0)$ against the reaction time demonstrates the pseudo-first-order kinetics characteristics of the oxidation of DBT using $Q_3H_3V_{10}O_{28}$.

To explain the mechanism of the aerobic oxidation of sulfur-containing compounds, UV-Vis spectrum of the reaction system was measured. An absorption band with λ_{max} = 231 nm is observed when $Q_3H_3V_{10}O_{28}$ is dissolved in decalin under nitrogen, as shown in Fig. 3. The band at 231 nm is attributed to ligand-to-metal charge-transfer. With introduction of molecular oxygen, the band at λ_{max} = 231 nm disappears and a new band appears at λ_{max} = 221 nm. This blue-shift upon introduction of molecular oxygen can be attributed to the formation of reactive intermediates.
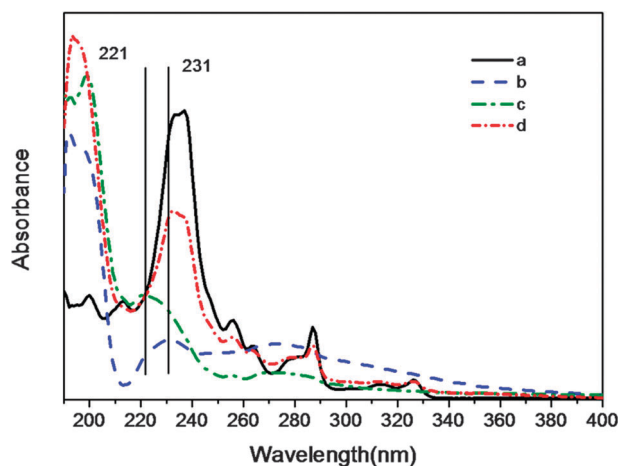

Fig. 3 UV-Vis spectra of $Q_3H_3V_{10}O_{28}$. All spectra were collected from 0.02 mmol L^{-1} solution (including $Q_3H_3V_{10}O_{28}$ and DBT). (a) DBT dissolved in decalin at 90 °C for 1 h. (b) $Q_3H_3V_{10}O_{28}$ dissolved in decalin at 90 °C for 1 h under 1 atm N_2. (c) $Q_3H_3V_{10}O_{28}$ dissolved in decalin after treatment with 1 atm O_2 at 90 °C for 1 h. (d) $Q_3H_3V_{10}O_{28}$ dissolved in decalin after addition of DBT at 90 °C for 1 h under 1 atm N_2.
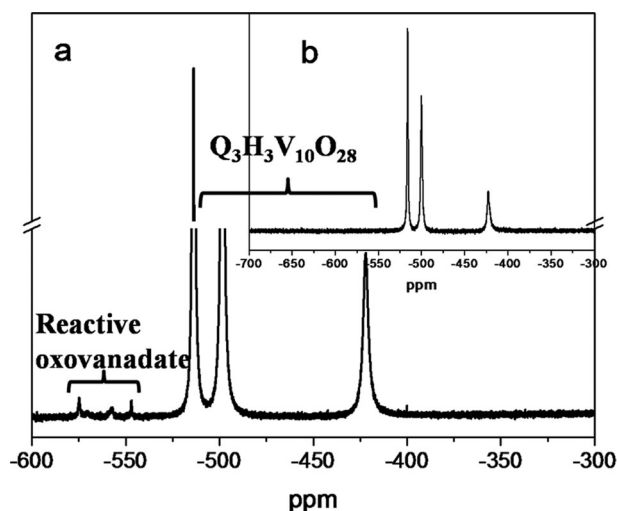

Fig. 4 (a) ^{51}V NMR spectrum of $Q_3H_3V_{10}O_{28}$ treated with O_2 in decalin; (b) ^{51}V NMR spectrum of $Q_3H_3V_{10}O_{28}$.

The absorption bands are similar with and without addition of DBT. These results suggest that the oxygen molecule coordinates to the catalyst decavanadates, and then the molecular oxygen is activated. When treated the catalysts with molecular oxygen in decalin, we observed that the color of the catalysts is changed from yellow to dark green. Three new peaks are detected in the ^{51}V NMR spectrum of the treated catalysts, as shown in Fig. 4. These 50–100 ppm decreases can be attributed to O^{2-} being replaced by $[OO]^{2-}$.[22,23] To further study the interaction between $Q_3H_3V_{10}O_{28}$ and molecular oxygen, we employed the ESR spin-trap technique with DMPO as traps. Fig. S2 (ESI†) shows the ESR signals from the *in situ* ODS process. No ESR signals were detected at 25 °C and 60 °C in the reaction system without the catalyst. With introduction of $Q_3H_3V_{10}O_{28}$, we still observe no ESR signal at 25 °C. Nevertheless, when the system was heated to 60 °C, a broad 6-line ESR signal was appeared. This sextet ESR signal observed can be assigned to the DMPO-$O_2^{\bullet-}$ adduct.[24–27] According to the *in situ* ESR signals, we can conclude that $O_2^{\bullet-}$ is generated by $Q_3H_3V_{10}O_{28}$ upon inter-action with molecular oxygen. The effect of $O_2^{\bullet-}$ on the reaction system using hydroquinone as a radical scavenger was also examined. There is almost no difference in conversion of DBT with or without hydroquinone (5 wt%) added in the system (see Fig. S3, ESI†). The result suggests that the oxidation of DBT to $DBTO_2$ was not through a radical chain mechanism. Therefore, a plausible mechanism is proposed as follows (Scheme 1).
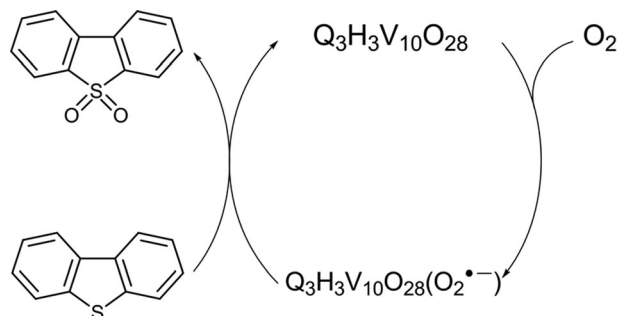
Scheme 1 Proposed mechanism for dioxygen activation and aerobic ODS.

First, the catalyst $Q_3H_3V_{10}O_{28}$ reacts with molecular oxygen to generate $O_2^{\bullet-}$, which reacts with $Q_3H_3V_{10}O_{28}$ to produce reactive oxovanadate species. Then, the reactive oxovanadate species oxidize DBT to $DBTO_2$.

In conclusion, the isopolyoxovanadate $[C_8H_{17}N(CH_3)_3]_3$-$H_3V_{10}O_{28}$ can interact with molecular oxygen in decalin to generate reactive oxovanadate species, which can oxidize DBT to $DBTO_2$ with high selectivity. It provides a new pathway for the ODS of diesel with molecular oxygen as an oxidant.

Notes and references

‡ Preparation of $[C_8H_{17}N(CH_3)_3]_3H_3V_{10}O_{28}$: sodium metavanadate, $NaVO_3$ (4.5 g, 37 mmol), was dissolved in H_2O (25 mL) at 60 °C. A solution of H_3PO_4 (6.2 mL, 1.5 M) was added to this vanadate solution with stirring. The pH value was adjusted to 5.5 by HNO_3 solution (1.5 M). The resulted dark red solution was treated with an aqueous solution of KCl (0.54 g) by gentle addition. Upon cooling, orange crystals of $K_3H_3V_{10}O_{28}$ precipitated from solution. $K_3H_3V_{10}O_{28}$ (1.08 g, 1 mmol) was dissolved in 15 mL of HCl (pH = 5.5) aqueous solution at 60 °C. An ethanolic solution (6 mL) with $C_{11}H_{26}NCl$ (0.62 g, 3 mmol) was added dropwise into the solution of $K_3H_3V_{10}O_{28}$ under stirring. A pale yellow precipitate was immediately formed. After continuously stirring for 2 h, the resulting mixture was centrifuged and dried at 60 °C in a vacuum for 24 h. IR (KBr, cm^{-1}): v = 956 (V–O$_t$), 825 (V–O$_b$), 752 (V–O$_b$), 600 (V–O$_b$), 530 (V–O$_b$). Oxidation of model sulfur-containing compounds: In a typical experiment, an oil bath was heated to 90 °C. The model sulfur-containing compound (DBT) was dissolved in 20 mL of decalin in a flask, in which the sulfur concentration was 500 ppm. 40 mg of $Q_3H_3V_{10}O_{28}$ was added to the solution under vigorous stirring with molecular oxygen bubbled through the reaction solution.

1 H. Lü, J. Gao, Z. Jiang, Y. Yang, B. Song and C. Li, *Chem. Commun.*, 2007, 150–152.
2 C. Song, *Catal. Today*, 2003, **86**, 211–263.
3 V. C. Srivastava, *RSC Adv.*, 2012, **2**, 759–783.
4 A. Rothlisberger and R. Prins, *J. Catal.*, 2005, **235**, 229–240.
5 A. Bosmann, L. Datsevich, A. Jess, A. Lauter, C. Schmitz and P. Wasserscheid, *Chem. Commun.*, 2001, 2494–2495.
6 Z. Jiang, H. Lü, Y. Zhang and C. Li, *Chin. J. Catal.*, 2011, **32**, 707–715.
7 J. M. Campos-Martin, M. C. Capel-Sanchez, P. Perez-Presas and J. L. G. Fierro, *J. Chem. Technol. Biotechnol.*, 2010, **85**, 879–890.
8 M. Te, C. Fairbridge and Z. Ring, *Appl. Catal., A*, 2001, **219**, 267–280.
9 T. Aida, D. Yamamoto, M. Iwata and K. Sakata, *Rev. Heteroat. Chem.*, 2000, **22**, 241–256.
10 S. Otsuki, T. Nonaka, N. Takashima, W. H. Qian, A. Ishihara, T. Imai and T. Kabe, *Energy Fuels*, 2000, **14**, 1232–1239.
11 P. De Filippis and M. Scarsella, *Energy Fuels*, 2003, **17**, 1452–1455.
12 B. Zhang, Z. Jiang, J. Li, Y. Zhang, F. Lin, Y. Liu and C. Li, *J. Catal.*, 2012, **287**, 5–12.
13 Y. Zhang, H. Lü, L. Wang, Y. Zhang, P. Liu, H. X. Han, Z. Jiang and C. Li, *J. Mol. Catal. A: Chem.*, 2010, **332**, 59–64.
14 Y. Zhang, L. Wang, Y. Zhang, Z. Jiang and C. Li, *Chin. J. Catal.*, 2011, **32**, 235–239.
15 C. Li, Z. X. Jiang, J. B. Gao, Y. X. Yang, S. J. Wang, F. P. Tian, F. X. Sun, X. P. Sun, P. L. Ying and C. R. Han, *Chem.–Eur. J.*, 2004, **10**, 2277–2280.
16 Y. Hangun, L. Alexandrova, S. Khetan, C. P. Horwitz, A. Cugini, B. Howard, D. D. Link and T. J. Collins, *J. Prepr. Am. Chem. Soc., Div. Pet. Chem.*, 2002, **47**, 42.
17 F. Zannikos, E. Lois and S. Stournas, *Fuel Process. Technol.*, 1995, **42**, 35–45.
18 J. Palomeque, J. M. Clacens and F. Figueras, *J. Catal.*, 2002, **211**, 103–108.
19 Y. Shiraishi, T. Hirai and I. Komasawa, *J. Chem. Eng. Jpn.*, 2002, **35**, 1305–1311.
20 A. Chica, A. Corma and M. E. Domine, *J. Catal.*, 2006, **242**, 299–308.
21 P. S. Tam, J. R. Kittrell and J. W. Eldridge, *Ind. Eng. Chem. Res.*, 1990, **29**, 321–324.
22 O. W. Howarth, *Prog. Nucl. Magn. Reson. Spectrosc.*, 1990, **22**, 453–485.
23 A. T. Harrison and O. W. Howarth, *J. Chem. Soc., Dalton Trans.*, 1985, 1173–1177.
24 L. Khachatryan, E. Vejerano, S. Lomnicki and B. Dellinger, *Environ. Sci. Technol.*, 2011, **45**, 8559–8566.
25 J. L. Clement, N. Ferre, D. Siri, H. Karoui, A. Rockenbauer and P. Tordo, *J. Org. Chem.*, 2005, **70**, 1198–1203.
26 Y. Cui, J. Huang, X. Fu and X. Wang, *Catal. Sci. Technol.*, 2012, **2**, 1396–1402.
27 Y. Cui, Z. Ding, P. Liu, M. Antonietti, X. Fu and X. Wang, *Phys. Chem. Chem. Phys.*, 2012, **14**, 1455–1462.