Oxidation of dibenzothiophene catalyzed by [C₈H₁₇N(CH₃)₃]₃H₃V₁₀O₂₈ using molecular oxygen as oxidant†

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

Received 5th September 2012, Accepted 16th October 2012
DOI: 10.1039/c2cc36482d

An isopolyoxovanadate catalyst [C₈H₁₇N(CH₃)₃]₃H₃V₁₀O₂₈ 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 ultra-deep 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 ppm W, 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. Oxidative desulfurization (ODS) as one of the most promising alternative technologies has attracted much attention. 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 H₂O₂–polyoxometalate, H₂O₂–formic-acid, H₂O₂–ionic liquids, H₂O₂–emulsion catalysts, H₂O₂–iron-complexes, H₂O₂–acetic-acid, H₂O₂–solid bases, H₂O₂–TiSi, and other non-hydrogen peroxide systems (e.g., tert-butyl hydroperoxide, NO₂, etc.). Those catalytic ODS processes based on H₂O₂ show high efficiency, but have disadvantages such as thermal instability (H₂O₂). Taking account of environmental, safety, and economic concerns, the utilization of O₂ 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 [C₈H₁₇N(CH₃)₃]₃H₃V₁₀O₂₈ (Q₃H₃V₁₀O₂₈ for short) under mild conditions. Oxidation of DBT-containing model oil was conducted in a flask with O₂ 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 (DBTO₂) (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 DBTO₂. We could obtain white needle-type crystals when the reaction system was cooled to room temperature, which are DBTO₂ (confirmed by the IR spectrum, see Fig. S1, ESI†). According to the above experiments, we can come to a conclusion that the DBT

![Figure 1](Fig. 1) Sulfur-specific GC-FPD chromatograms of the oxidation of DBT in decalin. Reaction conditions: Q₃H₃V₁₀O₂₈ (40 mg), DBT (S: 500 ppm) in 20 mL decalin, reaction temperature 90 °C, oxidant O₂ (1 atm).
present in decalin can be oxidized into DBTO$_2$ catalyzed by Q$_3$H$_3$V$_{10}$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$_3$H$_3$V$_{10}$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 $\lambda_{\text{max}} = 231$ nm is observed when Q$_3$H$_3$V$_{10}$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 $\lambda_{\text{max}} = 231$ nm disappears and a new band appears at $\lambda_{\text{max}} = 221$ nm. This blue-shift upon introduction of molecular oxygen can be attributed to the formation of reactive intermediates.

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]$_2^-$. To further study the interaction between Q$_3$H$_3$V$_{10}$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$_3$H$_3$V$_{10}$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$_2^-$ adduct. According to the in situ ESR signals, we can conclude that O$_2^-$ is generated by Q$_3$H$_3$V$_{10}$O$_{28}$ upon interaction with molecular oxygen. The effect of O$_2^-$ 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).
First, the catalyst Q₃H₁₇N(CH₃)₃H₃V₁₀O₂₈ reacts with molecular oxygen to generate O₂**, which reacts with Q₃H₁₇N(CH₃)₃H₃V₁₀O₂₈ to produce reactive oxovanadate species. Then, the reactive oxovanadate species oxidize DBT to DBTO₂.

In conclusion, the isopolyoxovanadate [C₈H₁₇N(CH₃)₃]₃H₃V₁₀O₂₈ can interact with molecular oxygen in decalin to generate reactive oxovanadate species, which can oxidize DBT to DBTO₂ with high selectivity. It provides a new pathway for the ODS of diesel with molecular oxygen as an oxidant.

We acknowledge the financial support from the National Nature Science Foundation of China (NSFC Grant no. 21173214).

Notes and references

† Preparation of [C₈H₁₇N(CH₃)₃]₃H₃V₁₀O₂₈: sodium metavanadate, NaVO₃ (4.5 g, 37 mmol), was dissolved in H₂O (25 mL) at 60 °C. A solution of H₃PO₄ (6.2 mL, 1.5 M) was added to this vanadate solution with stirring. The pH value was adjusted to 5.5 by HNO₃ solution (1.5 M). The resulted dark red solution was treated with NaVO₃ (4.5 g, 37 mmol), was dissolved in H₂O (25 mL) at 60 °C. The resulted dark red solution was treated with an aqueous solution of KCl (0.54 g) by gentle addition. Upon cooling, orange crystals of K₃H₃V₁₀O₂₈ precipitated from solution.

‡ A solution of H₃PO₄ (6.2 mL, 1.5 M) was added to this vanadate solution with stirring. The pH value was adjusted to 5.5 by HNO₃ 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 K₃H₃V₁₀O₂₈ precipitated from solution.

§ Calculation of V–O distances in K₃H₃V₁₀O₂₈: IR (KBr, cm⁻¹): 956 (V–O₄), 825 (V–O₃), 752 (V–O₃), 600 (V–O₄), 530 (V–O₃). Oxidation of model sulfur-containing compounds: In a typical experiment, an oil bath was heated to 90 °C. An ethanolic solution (6 mL) of C₁₁H₂₆NCl (0.62 g, 3 mmol) was added dropwise into the resulting mixture was centrifuged and dried at 60 °C in a vacuum for 24 h. IR (KBr, cm⁻¹): 956 (V–O₄), 825 (V–O₃), 752 (V–O₃), 600 (V–O₄), 530 (V–O₃). 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 Q₃H₁₇N(CH₃)₃H₃V₁₀O₂₈ was added to the solution under vigorous stirring with molecular oxygen bubbled through the reaction solution.