Oxidative desulfurization of dibenzothiophene with molecular oxygen using emulsion catalysis†

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Received (in Cambridge, UK) 24th July 2006, Accepted 29th September 2006
First published as an Advance Article on the web 26th October 2006
DOI: 10.1039/b610504a

Dibenzothiophene (DBT) is oxidized to the corresponding sulfoxide and sulfone in an emulsion system (W/O) composed of polyoxometalate anion $[C_{18}H_{37}N(CH_3)_3]_5[PV_2Mo_{10}O_{40}]$ as both the surfactant and catalyst, using molecular oxygen as the oxidant and aldehyde as the sacrificial agent under mild conditions.

In the last decade, much attention has been paid to the deep desulfurization of fuel oils due to more stringent environmental regulations. Although hydrodesulfurization (HDS) is highly efficient in removing thiols, sulfides, and disulfides, it is difficult to reduce refractory sulfur-containing compounds such as dibenzothiophene (DBT) and its derivatives, especially 4,6-dimethydibenzothiophene (4,6-DMDBT), to an ultra-low level. Therefore, it is highly desirable to develop non-HDS methods to meet the demands of producing clean diesel[1] with an extremely low concentration of sulfur-containing compounds. Among them, oxidative desulfurization combined with extraction is considered to be one of the most promising processes. Our previous work found that amphiphilic catalysts, $Q_3[PW_{12}O_{40}]$ and $Q_4[H_2NaPW_{10}O_{36}]$, assembled in an emulsion in diesel, could selectively oxidize sulfur-containing compounds into their corresponding sulfones by using an approximately stoichiometric amount of H_2O_2 as the oxidant. The sulfones can be readily separated from the diesel using an extractant and ultra-deep desulfurization of diesel can be achieved.[2]

However, the oxidation of these refractory sulfur-containing compounds using molecular oxygen instead of hydrogen peroxide as oxidizing agent under mild conditions has long been desired due to its low cost and green chemistry advantage. However, there are only a few reports on the oxidation of those refractory sulfur-containing compounds with molecular oxygen. Recently, cobalt salt and some metal oxide catalysts (including manganese and cobalt oxide) supported on γ-Al_2O_3 have been used as catalysts for the oxidation of sulfur-containing compounds with molecular oxygen.[3] In these processes, the sulfur compounds present in diesel can be oxidized to corresponding sulfones, which can be removed by subsequent adsorption or solvent extraction.

In this communication, we report the oxidation of dibenzothiophene (DBT) with molecular oxygen as the oxidant using an emulsion catalytic system where an amphiphilic catalyst $[C_{18}H_{37}N(CH_3)_3]_5[PV_2Mo_{10}O_{40}]$ acts as the surfactant. It is found that the mixture of MeCN and sulfur-containing molecules present in decalin can form an emulsion under stirring. The aldehyde and molecular oxygen dissolve in acetonitrile, inside the emulsion droplets, while the polyoxometalate anion $[C_{18}H_{37}N(CH_3)_3]_5$-$[PV_2Mo_{10}O_{40}]$ as both the surfactant and catalyst assembles on the interface of emulsion droplets. As a result, the acetonitrile, including isobutyl aldehydes, and molecular oxygen dissolved in acetonitrile is a disperse phase, and the decalin is thought of as a continuous phase in the emulsion system. DBT can be oxidized to the corresponding sulfoxide and sulfone in this emulsion system under mild conditions.

The oxidation of DBT present in MeCN was investigated firstly with amphiphilic catalyst $[C_{18}H_{37}N(CH_3)_3]_5[PV_2Mo_{10}O_{40}]$ using molecular oxygen as oxidant. Fig. 1 shows the sulfur-specific gas chromatography (GC) analyses before and after the catalytic oxidation of DBT in MeCN. DBT present in MeCN can be completely oxidized to sulfoxide and sulfones at 60 °C in 2 h, but the DBT present in decalin can not be oxidized at all (see ESI†). Thus, MeCN is considered to be one of the most suitable solvents for the oxidative desulfurization of diesel.[4] In order to oxidize DBT present in model diesel, MeCN was added to the reaction system. It was found that the emulsion droplets, which were

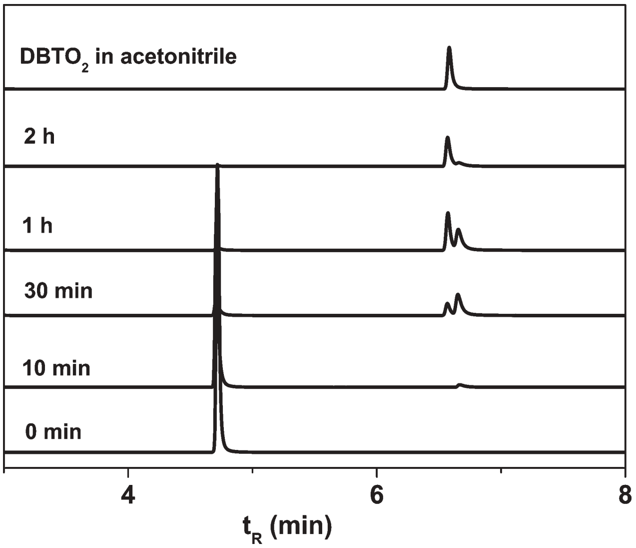

Fig. 1 Sulfur specific GC-FPD chromatograms for the oxidation of DBT with molecular oxygen/aldehyde in MeCN. (Conditions: $[C_{18}H_{37}N(CH_3)_3]_5PV_2Mo_{10}O_{40}$ 33 mg (0.01 mmol), DBT 147 mg (0.8 mmol) in 50 ml MeCN, isobutyraldehyde 0.72 ml (8 mmol), reaction temperature 60 °C.)

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† Electronic supplementary information (ESI) available: Synthesis and characterization of catalysts, oxidation of DBT, analysis of sulfur content and spectra. See DOI: 10.1039/b610504a

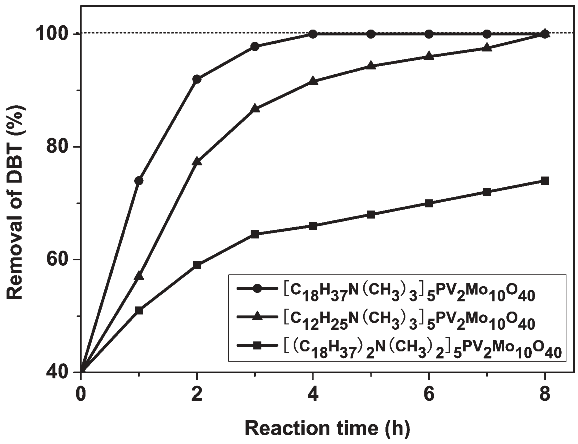


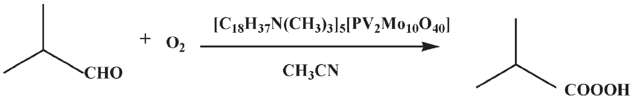
Fig. 2 Removal of DBT *vs.* reaction time in emulsion at 60 °C. (Conditions: $Q_5PV_2Mo_{10}O_{40}$ (0.01 mmol), DBT 147 mg (0. 8 mmol) in decalin, MeCN 50 ml, isobutyraldehyde 0.72 ml (8 mmol), reaction temperature 60 °C.)

composed of MeCN, decalin and amphiphilic catalyst $[C_{18}H_{37}N(CH_3)_3]_5[PV_2Mo_{10}O_{40}]$, could be formed under the conditions used, and the volume of emulsion was increased with increase of the volume of MeCN within a certain range.

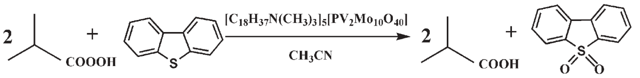
Three kinds of catalysts with different quaternary ammonium cations were synthesized to investigate the effect of the amphiphilic catalyst on the property and stability of the emulsion system. Fig. 2 shows the removal of DBT *vs.* reaction time ith three kinds of catalyst. Before reaction, about 40% DBT was transferred into the emulsion droplets (MeCN phase) from the decalin phase. During the process of oxidative reaction, the catalyst $[C_{18}H_{37}N(CH_3)_3]_5$-$[PV_2Mo_{10}O_{40}]$ exhibits more activity than the catalyst $[C_{12}H_{25}N(CH_3)_3]_5[PV_2Mo_{10}O_{40}]$. DBT was oxidized completely and efficiently removed from decalin phase in 4 h with the catalyst $[C_{18}H_{37}N(CH_3)_3]_5[PV_2Mo_{10}O_{40}]$. When the oxidation reaction was over, all DBT in MeCN and decalin had oxidized into DBT's sulfone, detected by GC-FPD. However, the catalyst $[(C_{18}H_{37}]_2N(CH_3)_2]_5PV_2Mo_{10}O_{40}$ shows low reaction activity, and after reaction the removal of DBT from model diesel was only 70%, even for 8 h.

The different catalytic performances of the three catalysts indicate that the quaternary ammonium cations in the catalysts play a vital role in the formation of the emulsion system. As is shown in Fig. 3, the catalyst $[C_{12}H_{25}N(CH_3)_3]_5[PV_2Mo_{10}O_{40}]$ with a shorter carbon chain has difficulty forming an emulsion, resulting in low conversion of DBT. The catalyst $[C_{18}H_{37}N(CH_3)_3]_5[PV_2Mo_{10}O_{40}]$ with a longer chain has high catalytic activity, as it can form relatively uniform emulsion droplets suspended in decalin phase. However, the catalyst $[(C_{18}H_{37}]_2N(CH_3)_2]_5PV_2Mo_{10}O_{40}$ shows low reaction activity despite the emulsion droplets being formed, possibly because the small emulsion droplets cannot supply enough oxidative sacrificial agent.

Aldehydes were known to be oxidized easily to corresponding peracids by molecular oxygen in the presence $PV_2Mo_{10}O_{40}{}^{-5}$.[5] Therefore, the oxidation of DBT to sulfoxide and sulfone with the dioxygen-$[C_{18}H_{37}N(CH_3)_3]_5PV_2Mo_{10}O_{40}$-aldehydes might proceed *via* the following two steps. First, the catalyst $[C_{18}H_{37}N(CH_3)_3]_5PV_2Mo_{10}O_{40}$ can continuously catalytically oxidize aldehyde to peracids with molecular oxygen on the interface of the emulsion droplets:



Then, the DBT was oxidized to sulfoxide and sulfone by isobutyl peracid on the emulsion droplets:



The amount of MeCN has a strong influence on the emulsion system. The ratio between MeCN and model diesel was tuned to optimize a suitable emulsion condition (see ESI†). DBT is not oxidized to sulfoxide or sulfone without MeCN; the conversion of DBT is increased with increasing volume of MeCN in emulsion, so the volume of emulsion was increased by reducing the ratio of oil to water (MeCN) in a certain range.[6] In addition, the sulfones can be separated directly from diesel to MeCN, and the oxidation and extraction can be finished simultaneously.

In summary, the catalyst $[C_{18}H_{37}N(CH_3)_3]_5PV_2Mo_{10}O_{40}$ assembled in emulsion droplets can oxidize DBT present in decalin to sulfoxide and sulfone using molecular oxygen as the oxidant and isobutyl aldehydes as the sacrificial agent, under mild conditions. The sulfones can be removed directly from diesel to MeCN and the oxidation and extraction can proceed simultaneously. These results demonstrate that the desulfurization of diesel oils *via* an oxidative desulfurization process with molecular oxygen as the oxidant is a possible process for ultra-deep desulfurization.

The authors are grateful for financial supported by the National Science Foundations of China (20503031 and 20673114).

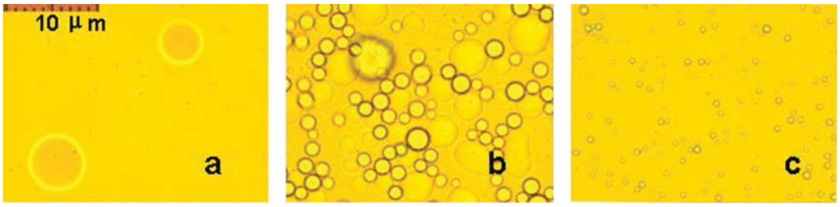


Fig. 3 Optical micrographs of the three emulsion systems. a: $[C_{12}H_{25}N(CH_3)_3]_5[PV_2Mo_{10}O_{40}]$; b: $[C_{18}H_{37}N(CH_3)_3]_5[PV_2Mo_{10}O_{40}]$; c: $[(C_{18}H_{37}]_2N(CH_3)_2]_5[PV_2Mo_{10}O_{40}]$.

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