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Achieving deep desulfurization with inverse-micellar polyoxometalates and oxygen†

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Designing green and efficient catalytic systems that can operate under mild conditions and utilize molecular oxygen as an oxidant for achieving deep desulfurization is highly desirable. In this study, an inverse-micellar polyoxometalate (POM) $(NH_4)_5(CTA)_6PMo_4V_8O_{40}$ (CTA = cetyltrimethylammonium), abbreviated as (CTA)PMo_4V_8, was designed and its activity in desulfurization was evaluated. Almost ∼100% of organic sulfur was removed in 8 h at 100 °C, using only flowing oxygen under atmospheric pressure. (CTA)PMo_4V_8 exhibited excellent activity in treating sulfur-containing compounds (dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (DMDBT), benzothiophene (BT) and thiophene) in real oils, *i.e.* diesel and FCC gasoline, affording clean oils with super-low sulfur content of 8.77 and 6.17 ppm, respectively. Furthermore, (CTA)PMo_4V_8 showed high activity in the oxidative desulfurization of real oils in the presence of oxygen and nitrogen (volume ratio 1 : 1). Such inverse-micellar POMs could be reused at least six times without significant loss of activity due to their high stability.

1 Introduction

Although great efforts have been dedicated to developing desulfurization techniques for fossil fuels,[1,2] methods that can achieve super-clean oils with a sulfur content of lower than 10 ppm are still needed due to strict regulations and environmental problems caused by the use of fossil fuels.[3] Several desulfurization methods have been developed, including hydrodesulfurization,[1] adsorption,[2] extractive desulfurization,[4,5] and oxidative desulfurization.[6,7] In order to obtain super-clean oils, oxidative desulfurization (ODS) is a good choice, due to its advantages of high efficiency and low cost, especially for the removal of aromatic sulfur compounds such as dibenzothiophene (DBT), 4,6-dimethyldibenzothiophene (DMDBT), benzothiophene (BT) and thiophene. Recently, various ODS methods have been developed using H_2O_2, O_2 or other oxidants, while O_2 or air is more economical. Generally, achieving aerobic ODS under mild conditions is still a challenge. Moreover, the combination of oxidation of refractory aromatic sulfur and

extraction of obtained sulfone in one unit is more efficient, cheap and environmentally benign.

Polyoxometalates (POMs) have been widely investigated as potential catalysts in aerobic oxidation desulfurization (Table S1†). In this study, POMs and POM-supported hybrids were evaluated for their oxidation of DBT, BT and 4,6-DMDBT at 60–120 °C for 1.5–12 h, and were found to give 70–100% conversion. 100% conversion of DBT, 4,6-DMDBT, and BT was achieved using $(NH_4)_5H_6PMo_4V_8O_{40}$ at 100 °C for 6–11 h with TOF values of 6.76, 5.87, 5.07 h^{-1} (TOF = [converted sulfur]/[usage of POMs] × time (h^{-1})). Meanwhile, the oxidation of thiophene was successfully performed at 100 °C for 12 h using $(NH_4)_5$-$H_6PMo_4V_8O_{40}$ with a TOF of 7.18 h^{-1}. Compared to $(NH_4)_5$-$H_6PMo_4V_8O_{40}$, $H_4PMo_{11}VO_{40}$ exhibited lower activity or 17.3% removal efficiency under the same reaction conditions (Table S1†). This determined that POMs containing more vanadium atoms exhibited higher activity than those with fewer. In the aerobic oxidation of refractory aromatic sulfur compounds, there were difficulties in achieving mass transfer between solid POMs, gaseous O_2 and substrates, which limited the oxidation rates. One strategy to overcome these drawbacks is to design an amphiphilic POM system, which uses a long-chain surfactant as a counter-ion to fabricate surfactant/POMs anion–cation hybrids.[8,9] In organic solvents, such amphiphilic molecules can self-assemble to form inverse-micelles, which can concentrate O_2 and substrates to enhance the reaction rates.[10]

In the course of our research work, $(NH_4)_5H_6PMo_4V_8O_{40}$ was found to be most active in the aerobic oxidation of DBT and its derivates. However, there were some difficulties in mass transfer between the solid catalyst, oil and oxygen. During our study

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on POM catalysis, it was found that amphiphilic POMs could concentrate organic substrates and oxygen around the active sites of POMs to enhance the activity.[8,9]

In order to solve the environmental problems caused by fossil fuels, there is an urgent need for a green and efficient catalytic system that can obtain super-clean oil under mild conditions, using molecular oxygen as an oxidant. Therefore, the amphiphilic POM $(NH_4)_5(CTA)_6PMo_4V_8O_{40}$ (CTA is cetyl-trimethylammonium, abbreviated as $(CTA)PMo_4V_8$) was synthesized and was used as a catalyst in the ODS of organic sulfur compounds under atmospheric pressure. In previous research, the ODS of real fuels has rarely been reported. This process is important in the production of ultra-clean oils. $(CTA)PMo_4V_8$ showed high activity in treating diesel and FCC gasoline with 8.77 and 6.17 ppm sulfur content, which meets the VI standard of China.[11] The regeneration and stability of $(CTA)PMo_4V_8$ was also assessed to determine its economic viability.

2 Experimental

Details about the materials and physical measurements are given in the ESI,† while the experimental methods are also described.

3 Results and discussion

3.1 Synthesis and characterization

$(CTA)PMo_4V_8$ was characterized firstly by elementary analysis to give the elemental content as: Mo, 11.75%; P, 0.96%; V, 12.52%; C, 42.01%; N, 4.74%; H, 8.33%. These results are consistent with the calculated values of: Mo, 11.79%; P, 0.90%; V, 12.53%; C, 42.00%; N, 4.70%; H, 8.30%. They also correspond to the formula of $(NH_4)_5(CTA)_6PMo_4V_8O_{40}$, and give a P : Mo : V molar ratio of 1 : 4 : 8, indicating that the Keggin anion is intact. Meanwhile, the carbon content and nitrogen content in the POM were about 42.01% and 4.74%, respectively, corresponding to 6 moles of CTA cation in the hybrid. The IR spectrum (Fig. S1†) of $(CTA)PMo_4V_8$ shows four characteristic peaks, at 1051 cm^{-1} ($\nu_{as_{P-Oa}}$), 930 cm^{-1} ($\nu_{as_{Mo-Od}}$), 863 cm^{-1} ($\nu_{as_{Mo-Ob}}$), and 743 cm^{-1} ($\nu_{as_{Mo-Oc}}$), which are similar to its parent,

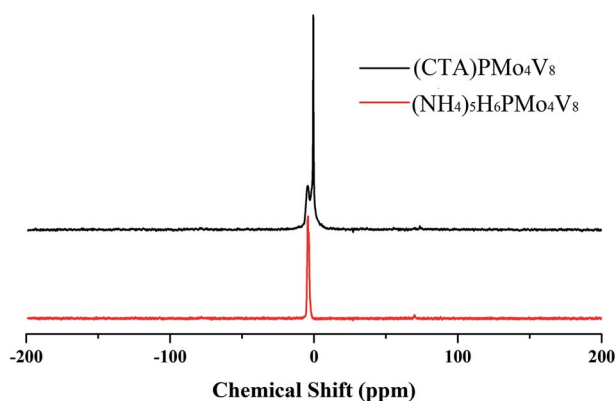$(NH_4)_5H_6PMo_4V_8$ (1055, 932, 861 and 732 cm^{-1}). The presence of these four characteristic peaks with slight shifts indicates that the Keggin structure is maintained and there is some interaction between $(CTA)^+$ and $PMo_4V_8^{11-}$. The ^{31}P MAS NMR of $(CTA)PMo_4V_8$ exhibits one peak at -4.43 ppm with a shoulder (Fig. 1). Compared to the peak of $(NH_4)_5H_6PMo_4V_8$ at -4.44 ppm, it exhibits a slight shift and a shoulder due to some interaction between CTA^+ and $PMo_4V_8^{11-}$. XPS was used to determine the composition and valence states of $(CTA)PMo_4V_8$ (Fig. 2). From the XPS results, it can be seen that Mo_{3d} and V_{2p} at 243.3 and 527.8 eV were found, corresponding Mo^{6+}, V^{5+} and P^{5+}, indicating the existence of the PMo_4V_8 anion in the hybrid. Meanwhile, C1s, O1s and N1s were also found in the XPS results due the existence of CTA^+ and NH_4^+ cations.

The morphology of $(CTA)PMo_4V_8$ in decalin was determined using SEM (Fig. S3†). It can be seen that spheres were found, with a size of 1.0×10^3 nm, showing that $(CTA)PMo_4V_8$ could

Fig. 2 XPS spectra of CTAB, $(NH_4)_5H_6PMo_4V_8$ and $(CTA)PMo_4V_8$.

Fig. 1 The ^{31}P MAS NMR spectra of $(NH_4)_5H_6PMo_4V_8$ and $(CTA)PMo_4V_8$.
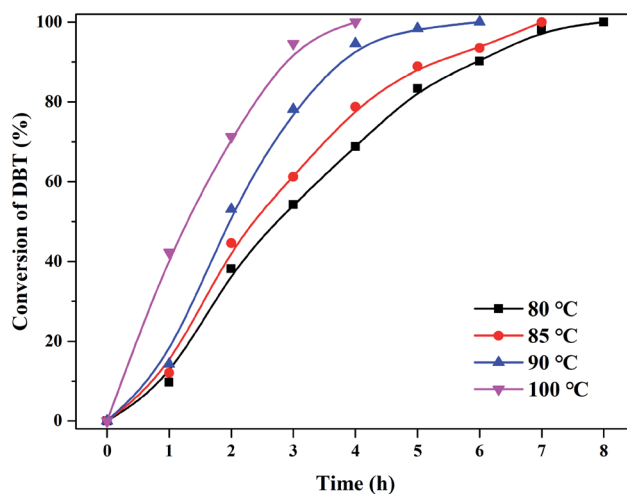
Fig. 3 The effect of temperature from 80 °C to 100 °C on DBT removal in the presence of $(CTA)PMo_4V_8$ (0.05 mmol) with O_2, 5 h.

$$(NH_4)_5H_6PMo_4V_8O_{40} + 6\ CTAB \longrightarrow (CTA)_6(NH_4)_5PMo_4V_8O_{40}$$

decalin
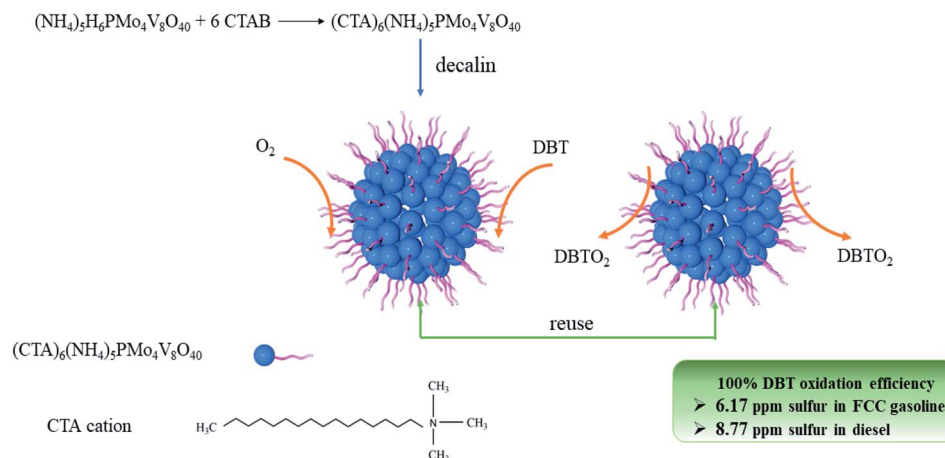
Scheme 1   Illustration of the adsorption of DBT by $(CTA)PMo_4V_8$.

self-assemble to form inverse-micelles. As shown in Fig. S4,† $(CTA)PMo_4V_8$ presents a long-range ordered regular arrangement in a parallel direction. A combination of elementary analysis, IR, ^{31}P MAS NMR, XPS, SEM and TEM determined that $(CTA)PMo_4V_8$ maintained the Keggin structure, while the interaction between CTA^+ and $PMo_4V_8^{11-}$ confirmed its self-assembly to form inverse-micelles in decalin.

3.2   Catalytic properties

The activity of $(CTA)PMo_4V_8$ in the ODS of DBT was assessed using only flowing oxygen under atmospheric pressure (Fig. 3). It can be seen that $(CTA)PMo_4V_8$ could activate O_2 to oxidize DBT in the temperature range of 80 °C to 100 °C. The maximum conversion of DBT was obtained as ~100% at 4, 6, 7, and 8 h at different reaction temperatures of 100, 90, 85 and 80 °C, respectively. Based on these results, the activation energy (E_a) was calculated as 45.38 kJ mol^{-1} (Fig. S5†). Compared to $(NH_4)_5H_6PMo_4V_8$, the E_a and TOF of $(CTA)PMo_4V_8$ for the aerobic oxidation of DBT were improved from 2690.49 kJ mol^{-1} and 6.76 h^{-1} to 45.38 kJ mol^{-1} and 13.89 h^{-1}.[7] This improvement might be due to the self-assembly of $(CTA)PMo_4V_8$ in decalin, as CTA^+ cations wrap around active $PMo_4V_8^{11-}$ cations, providing concentrated active sites for DBT (Scheme 1). Meanwhile, the adsorption of DBT by $(CTA)PMo_4V_8$ and $(NH_4)_5$-$H_6PMo_4V_8$ varied from 40.9% to 32.6% under the same reaction conditions, when using nitrogen instead of oxygen for 30 min at 100 °C. The selectivity of DBT oxidation was almost 100% to sulfone ($DBTO_2$), as determined by GC-MS (Fig. S6†). The concentration of DBT also influenced the activity of (CTA) PMo_4V_8, as shown by increasing DBT concentration from 50 to 500 ppm (Fig. S7†), whereby 100% conversion was easily achieved at 50 ppm of DBT. Achieving 100% conversion at 50 ppm of DBT demonstrated the ability of $(CTA)PMo_4V_8$ to treat organic sulfur at low concentrations. Another advantage for $(CTA)PMo_4V_8$ is that produced $DBTO_2$ can be repelled from the active sites of PMo_4V_8 by the hydrophobic surrounding of surfactant tails (Fig. S8†). From Fig. S8,† it can be seen that the

obtained crystal of $DBTO_2$ was found to be attached to the reactor, and needed to be separated using a decanting method.

Meanwhile, $(CTA)PMo_4V_8$ showed wide tolerance to different substrates, including 4.6-DMDBT and BT (Fig. 4). Without any catalyst, no desulfurization of organic sulfur was found, showing the limitation of oxygen under such reaction conditions. It can be seen that the oxidation of various organic sulfur compounds depends on the sulfur electron density: 5.758, 5.758 and 5.760 corresponding to BT, DBT and 4.6-DMDBT, respectively. The activity followed the trend of DBT > 4.6-DMDBT > BT with a reaction time of 5 h. Up until now, there are few reports concerning the aerobic oxidation of thiophene (Table S1†). $(CTA)PMo_4V_8$ could activate O_2 to oxidize thiophene with almost 100% conversion at elevated temperatures from 90 to 110 °C (Fig. 4).

Based on the above results, $(CTA)PMo_4V_8$ was expected to be effective in the ODS treatment of real oils containing high amounts of sulfur compounds. The ODS of diesel (1282 ppm sulfur content) and FCC gasoline (996 ppm sulfur content) was performed under the reaction conditions of 6 mL of oil and 0.05 mmol of catalyst for 8 h with stirring (500 rpm) at 100 °C with flowing molecular oxygen at 10 mL min^{-1}. Ultra-clean oils were obtained with sulfur content of 6.17 and 8.77 ppm, exhibiting 99.1% and 99.5% removal efficiency, respectively, using O_2 as an oxidant under atmospheric pressure. In order to improve the safety, a mixture of oxygen and nitrogen with a volume ratio of 1 : 1 was used instead of pure oxygen. (CTA) PMo_4V_8 demonstrated 87.6% and 89.4% desulfurization efficiency in diesel and FCC gasoline treatment, respectively, demonstrating its potential application in the industry.

The reusability of a catalytic system is vital, and determines its usability in practical applications.[12] Therefore, the spent catalyst was separated from the reaction system together with obtained $DBTO_2$ by filtration after the completion of each run, and was washed with ethanol to separate $DBTO_2$ for reuse. $(CTA)PMo_4V_8$ was found to be capable of catalyzing the oxidation of DBT for ten reaction cycles without a significant decrease of its activity (Fig. 5). The loss of $(CTA)PMo_4V_8$ was only about 8.3% of the initial amount after ten cycles. This loss of catalyst
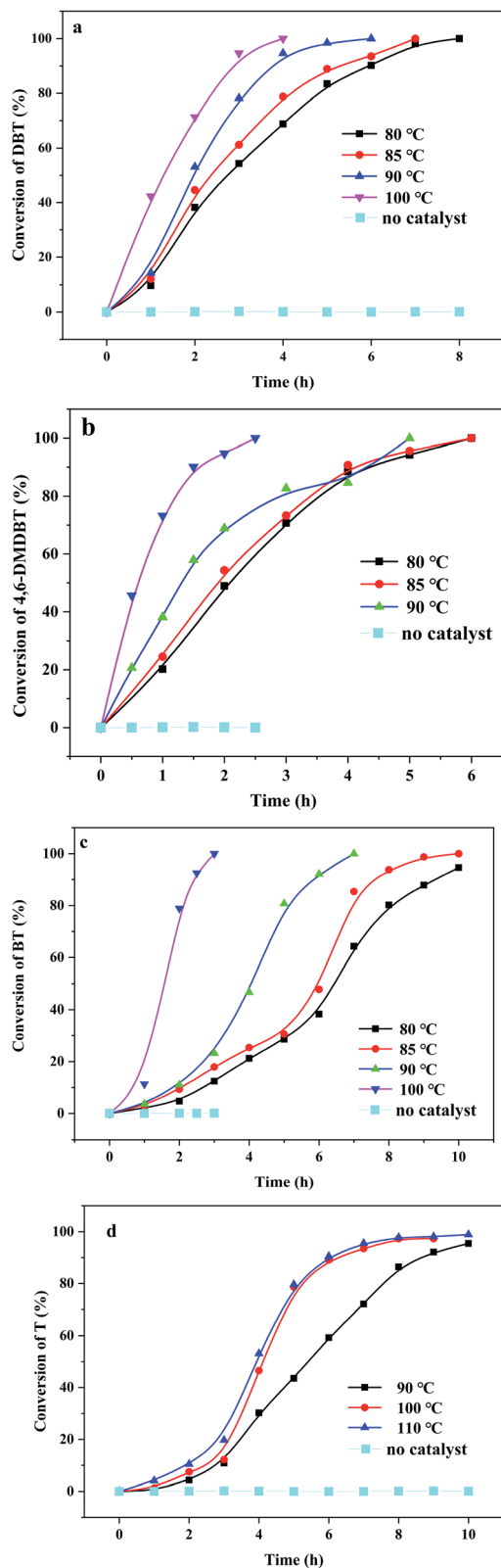
Fig. 4 Different organic sulfur compounds in the presence of (CTA) PMo_4V_8 (0.03 mmol) with O_2: (a) DBT; (b) 4,6-DMDBT; (c) BT; and (d) T.

Fig. 5 Reusability of (CTA)PMo_4V_8. Reaction conditions: DBT (500 ppm, 6 mL decalin), (CTA)PMo_4V_8 (0.05 mmol) at 100 °C with O_2, 5 h.

PMo_4V_8 was determined by IR, XPS and SEM (Fig. S9†), which showed that the spent catalyst (CTA)PMo_4V_8 displayed similar characteristics to the fresh one. The above results confirmed that (CTA)PMo_4V_8 remained intact during reaction and exhibits long durability and stability for practical applications.

4 Conclusions

(CTA)PMo_4V_8 exhibits a high efficiency both in the oxidation of model oils and real oils, through the synergistic effect of concentrating DBT around active sites, activating O_2, and repelling $DBTO_2$ from $PMo_4V_8^{11-}$ under atmospheric pressure. Almost 100% efficiency was achieved in the treatment of DBT, BT, 4,6-DMDBT and thiophane, while two kinds of ultra-clean oils with 8.77 and 6.17 ppm were obtained using (CTA)PMo_4V_8 and O_2. (CTA)PMo_4V_8 showed high stability and excellent recycling performance, and great potential for desulfurization using O_2 or a mixture of oxygen and nitrogen under atmospheric pressure.

Author contributions

Jinghui Wu, Yang Huo and Xianze Wang conceived and designed the experiments; Jinghui Wu, Yue Li and Xianze Wang performed the experiments; Yue Li and Menting Jiang analyzed the data; Jinghui Wu and Yue Li contributed analysis tools; Jinghui Wu, Xianze Wang and Xiaohong Wang wrote the paper. Yang Huo and Xianze Wang have given their approval for the final version of the manuscript.

Conflicts of interest

There are no conflicts to declare.

Acknowledgements

was due to operation during separation or washing treatment. It was confirmed that (CTA)PMo_4V_8 is relatively stable and recyclable under extremely mild conditions. The stability of (CTA)
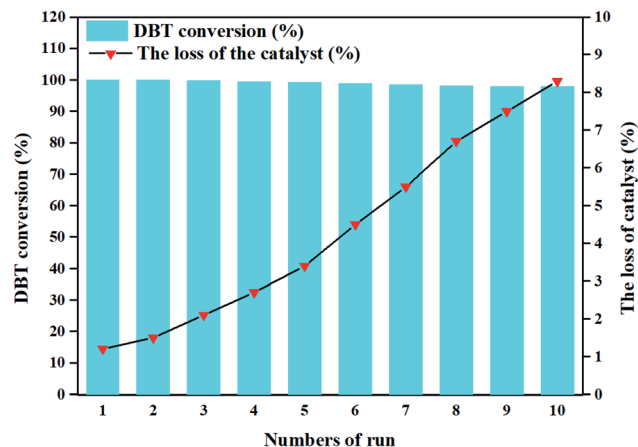

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