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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) $(\text{NH}_4)_5(\text{CTA})_6\text{PMo}_4\text{V}_8\text{O}_{40}$ (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.

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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,⁴ 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 $(\text{NH}_4)_5\text{H}_6\text{PMo}_4\text{V}_8\text{O}_{40}$ 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 $(\text{NH}_4)_5\text{H}_6\text{PMo}_4\text{V}_8\text{O}_{40}$ with a TOF of 7.18 h^{-1} . Compared to $(\text{NH}_4)_5\text{H}_6\text{PMo}_4\text{V}_8\text{O}_{40}$, $\text{H}_4\text{PMo}_{11}\text{VO}_{40}$ 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, $(\text{NH}_4)_5\text{H}_6\text{PMo}_4\text{V}_8\text{O}_{40}$ was found to be most active in the aerobic oxidation of DBT and its derivatives. 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 $(\text{NH}_4)_5(\text{CTA})_6\text{PMo}_4\text{V}_8\text{O}_{40}$ (CTA is cetyltrimethylammonium, abbreviated as $(\text{CTA})\text{PMo}_4\text{V}_8$) 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. $(\text{CTA})\text{PMo}_4\text{V}_8$ 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 $(\text{CTA})\text{PMo}_4\text{V}_8$ 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

$(\text{CTA})\text{PMo}_4\text{V}_8$ 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 $(\text{NH}_4)_5(\text{CTA})_6\text{PMo}_4\text{V}_8\text{O}_{40}$, 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 $(\text{CTA})\text{PMo}_4\text{V}_8$ shows four characteristic peaks, at 1051 cm^{-1} ($\nu_{\text{asP-Oa}}$), 930 cm^{-1} ($\nu_{\text{asMo-Od}}$), 863 cm^{-1} ($\nu_{\text{asMo-Ob}}$), and 743 cm^{-1} ($\nu_{\text{asMo-Oc}}$), which are similar to its parent,

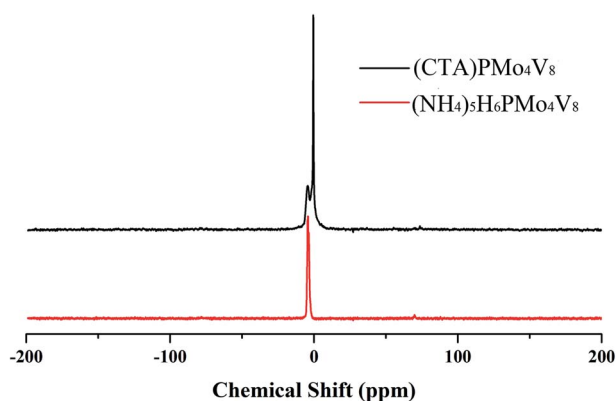


Fig. 1 The ^{31}P MAS NMR spectra of $(\text{NH}_4)_5\text{H}_6\text{PMo}_4\text{V}_8$ and $(\text{CTA})\text{PMo}_4\text{V}_8$.

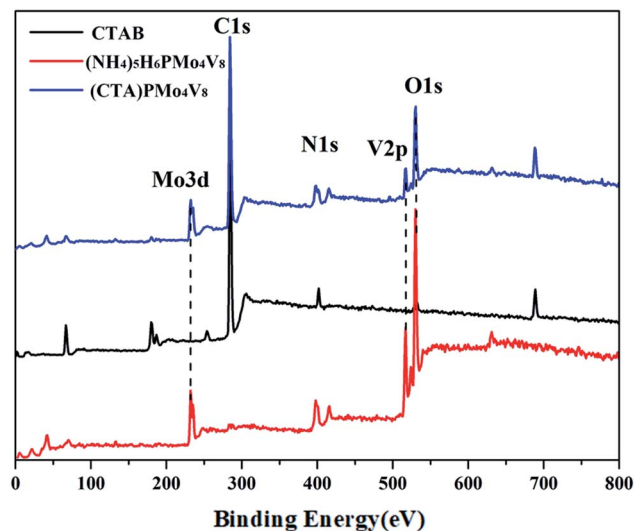


Fig. 2 XPS spectra of CTAB, $(\text{NH}_4)_5\text{H}_6\text{PMo}_4\text{V}_8$ and $(\text{CTA})\text{PMo}_4\text{V}_8$.

$(\text{NH}_4)_5\text{H}_6\text{PMo}_4\text{V}_8$ ($1055, 932, 861$ 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 $(\text{CTA})^+$ and $\text{PMo}_4\text{V}_8^{11-}$. The ^{31}P MAS NMR of $(\text{CTA})\text{PMo}_4\text{V}_8$ exhibits one peak at -4.43 ppm with a shoulder (Fig. 1). Compared to the peak of $(\text{NH}_4)_5\text{H}_6\text{PMo}_4\text{V}_8$ at -4.44 ppm , it exhibits a slight shift and a shoulder due to some interaction between CTA^+ and $\text{PMo}_4\text{V}_8^{11-}$. XPS was used to determine the composition and valence states of $(\text{CTA})\text{PMo}_4\text{V}_8$ (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, C_{1s} , O_{1s} and N_{1s} were also found in the XPS results due the existence of CTA^+ and NH_4^+ cations.

The morphology of $(\text{CTA})\text{PMo}_4\text{V}_8$ in decalin was determined using SEM (Fig. S3[†]). It can be seen that spheres were found, with a size of $1.0 \times 10^3\text{ nm}$, showing that $(\text{CTA})\text{PMo}_4\text{V}_8$ could

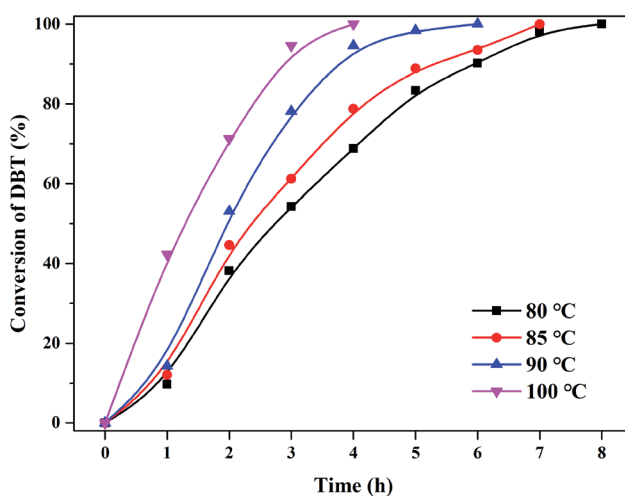
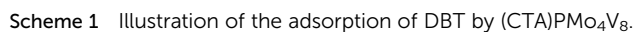


Fig. 3 The effect of temperature from $80\text{ }^\circ\text{C}$ to $100\text{ }^\circ\text{C}$ on DBT removal in the presence of $(\text{CTA})\text{PMo}_4\text{V}_8$ (0.05 mmol) with O_2 , 5 h .





3.2 Catalytic properties

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 DBTO₂ by filtration after the completion of each run, and was washed with ethanol to separate DBTO₂ for reuse. (CTA)PMo₄V₈ 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)PMo₄V₈ was only about 8.3% of the initial amount after ten cycles. This loss of catalyst

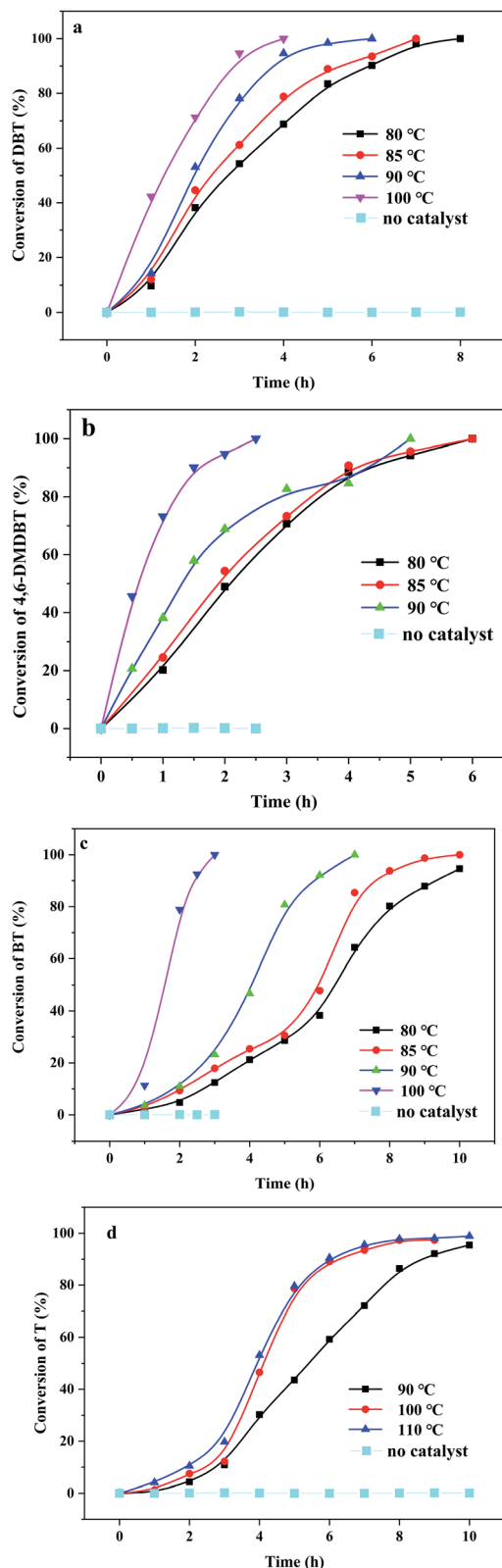


Fig. 4 Different organic sulfur compounds in the presence of (CTA)PMo₄V₈ (0.03 mmol) with O₂: (a) DBT; (b) 4,6-DMDBT; (c) BT; and (d) T.

was due to operation during separation or washing treatment. It was confirmed that (CTA)PMo₄V₈ is relatively stable and recyclable under extremely mild conditions. The stability of (CTA)

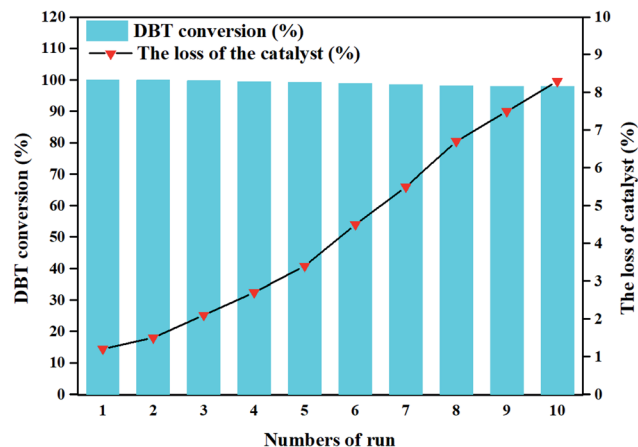


Fig. 5 Reusability of (CTA)PMo₄V₈. Reaction conditions: DBT (500 ppm, 6 mL decalin), (CTA)PMo₄V₈ (0.05 mmol) at 100 °C with O₂, 5 h.

PMo₄V₈ was determined by IR, XPS and SEM (Fig. S9[†]), which showed that the spent catalyst (CTA)PMo₄V₈ displayed similar characteristics to the fresh one. The above results confirmed that (CTA)PMo₄V₈ remained intact during reaction and exhibits long durability and stability for practical applications.

4 Conclusions

(CTA)PMo₄V₈ 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 O₂, and repelling DBTO₂ from PMo₄V₈^{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)PMo₄V₈ and O₂. (CTA)PMo₄V₈ showed high stability and excellent recycling performance, and great potential for desulfurization using O₂ 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.

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