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Kinetics of the oxidation of benzothiophene to H_2SO_4 with aqueous P-Mo-V-heteropolyacids and VO_2^+ as catalyst and molecular oxygen in biphasic extractive oxidative desulphurisation.

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Highlights

- Sulfuric acid is the main product of EODS with molybdovanadophosphate catalysts (HPA-n).
- VO_2^+ is the active catalyst; HPA-n regenerates VO_2^+-catalyst, closing the catalytic cycle.
- Kinetic models for all three partial (oxidation-) steps are given.
- Substrate oxidation is rate determining step; overall kinetic model is given.

1. Introduction

Crude oil contains considerable amounts of organic sulphur compounds. The maximum amount of sulphur in fuels is regulated by law to 10 ppmw [1], making desulphurisation a crucial step in the refining industry. Here, hydrodesulphurisation (HDS) is the process of choice. However, in this process, dibenzothiophenes are only partly removed [2]. Consequently, there is a wide interest in improving desulphurisation; here, oxidative desulphurisation (ODS) appears to be promising, since ODS leads to good conversions at rather low temperatures (< 130 °C) and pressures (< 30 bar).

Polyoxometalates (POMs) are widely used for oxidation reactions. In particular, Keggin-type POM catalysts, such as $H_{3+n}[PMo_{12-n}V_nO_{40}]$ = HPA-n, are used in catalytic liquid-phase oxidation. Besides hydrogen peroxide, only few publications deal with dioxygen as oxidant although it is very cheap (when air is used) and environmentally benign. The HPA-n catalyst is working as an efficient reversible redox system as the catalyst oxidises the substrate (sulphur compound), is in turn reduced, and reoxidized by O_2.

2. Methods

We have investigated the POM-catalysed EODS of model oil (isooctane containing benzothiophene (BT)) and HPA-5, HPA-1/VO_2^+ as catalysts. The EODS is performed as biphasic process with water as green solvent forming the second phase, which contains the catalysts and acts as extracting solvent for products. In addition, O_2 is used as oxidant. (Fig. 1 left.) The catalyst is monitored by means of Cyclic Voltammetry, ^{31}P-NMR, and UV-VIS spectroscopy, revealing its conditions at different pH-values.

3. Results and discussion

At temperatures up to 120 °C and dioxygen pressures up to 20 bar, BT is oxidised mainly to H_2SO_4 and water-soluble sulphur-organic acidic compounds (Fig. 1 right) leading to an in-situ extraction of the products into the aqueous phase (Fig. 1 left). Hence, downstream extraction of the model oil is unnecessary, avoiding hazardous organic extraction agents.

Experimental data reveal that HPA-5 shows a distinct running-in characteristic taking up to 3 hours (Fig. 2 top left); this period is due to the dissociation of the HPA-5 yielding pervanadyl ions (VO_2^+; active catalyst) and HPA-n with lower vanadium contents (n<5). The dissociation rate depends on the pH-value at the beginning of the reaction (pH is about 2.2 with c(HPA) = 2.5 mmol l^{-1}) and, therefore, on the concentration of the acidic catalyst in the aqueous phase (Fig. 2 top right). At pH-values below 2.0, VO_2^+ is released faster, thereby the running-in time is decreased. However, the reaction is hindered at pH-values below 1.5; this is expressed in poor reaction rates, leading to an optimum pH-window between 1.5 and 2.0 for the EODS.

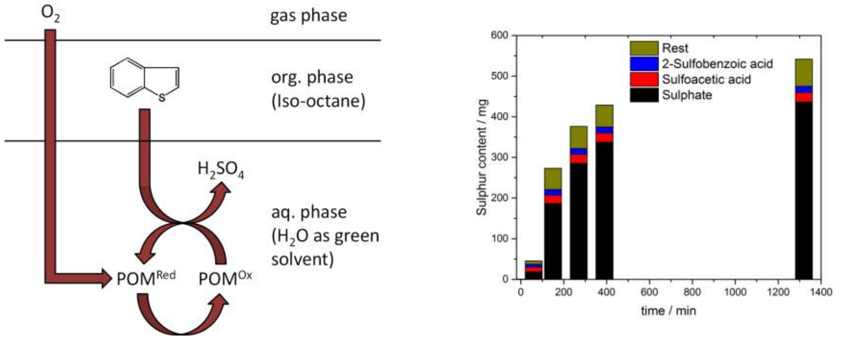

Figure 1. (left) Extractive Oxidative Desulphurisation with Polyoxometalate (POM) catalysts; (right) Distribution of products for EODS (120°C, 17.5bar oxygen, 2.5 mmol l^{-1} HPA-5, c(BT) = 11000 ppmw)

By using HPA-1 (which is not active used as catalyst alone) in combination with $VOSO_4$ as catalytic-system, the running-in time is avoided even at pH-values above 2.0. The HPA-1 directly oxidizes the VO^{2+} ion into the VO_2^+ ion. At T = 45°C and $p(O_2)$ = 17.5bar, >90% conversion is obtained after 30 min; this indicates that reoxidation of the vanadyl ion is not the rate-determining step in the oxidation process. In addition, kinetic data reveal that the reoxidation of HPA-1 is very fast with dioxygen. In this contribution, the kinetics of HPA-1 reoxidation with O_2 as well as the kinetics of vanadyl oxidation by HPA-1 and by O_2 are presented; finally, the kinetics of the substrate oxidation is given (Fig. 2 bottom). Combining the individual kinetic models, full modelling of the process is possible.

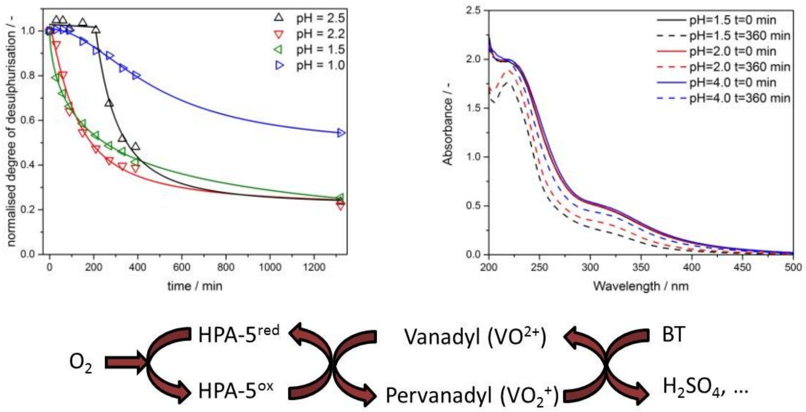

Figure 2. (top left) normalised degree of desulphurisation at different starting pH-values (120°C, 17.5bar oxygen, 2.5 mmol l^{-1} HPA-5, c(BT) = 11000 ppmw); (top right) UV-VIS spectra of HPA-5 in aqueous solution at different pH-values as a function of time; (bottom) catalytic system for EODS of benzothiophene (BT);

4. Conclusions

Molybdovanadophosphate heteropolyacids and pervanadyl ion are versatile catalysts for the oxidative desulphurisation of benzothiophene. With optimised reactions conditions, 100% conversion is obtained within 2 hours. As active catalyst species responsible for the oxidation of BT, the VO_2^+ ion is suggested, wheras the HPA-1 holds for the regeneration of pervandyl; finally, HPA-1 is reoxidised by dioxygen, closing the catalytic cycle. For the three individual reactions, kinetic parameters have been determined resulting in an overall reaction model.

References

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Keywords
polyoxometalate; EODS; two-phase catalysis; reaction kinetics;