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Polyisobutylene oligomer-bound polyoxometalates as efficient and recyclable catalysts for biphasic oxidations with hydrogen peroxide†

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Polyisobutylene (PIB) oligomer-bound amines render Keggin polyoxometalates (POM) heptane soluble, making them efficient and recyclable catalysts for environmentally benign biphasic oxidations with hydrogen peroxide. This is illustrated using both oxidative desulfurization and alkene epoxidation reactions that can be efficiently carried out in a heptane-water two-phase system occurring through facile phase transfer of POM by the amine terminated PIB oligomer.

Polyoxometalates (POMs), comprising O-sharing MO_x polyhedra (most often $M = Mo^{VI}$ and W^{VI}), have found applications in various disciplines,^{1,2} of which catalysis is by far the most important. This includes large-scale industrial processes such as the oxidation of methacrolein to methacrylic acid, the hydration of alkenes to alcohols and the synthesis of ethyl acetate by direct addition of acetic acid to ethylene.^{2e}

It has been extensively documented that POMs, especially those comprising Keggin type polyanions $[XM_{12}O_{40}]^{m-}$ ($X = P^V$ ($m = 3$) and Si^{IV} ($m = 4$)), serve as precursors of highly efficient catalysts for environmentally benign biphasic oxidations with hydrogen peroxide. Here we look at two reactions of significant practical importance – oxidative desulfurization³ and olefin epoxidation.⁴ Both are catalyzed by POMs in homogeneous or two-phase systems and are the subject of much current interest. There is compelling evidence that Keggin polyanions are transformed by excess H_2O_2 in solution to form peroxo polyoxometalate species, e.g. $\{PO_4[WO(O_2)_2]_4\}^{3-}$, which have been suggested to be the active intermediates in oxidations with H_2O_2 .¹¹ Biphasic oxidations in a water–organic system are particularly attractive, as such systems facilitate product/catalyst separation. These reactions typically involve phase-transfer catalysis with peroxo polyanion transport through the water–organic interface and require an efficient agent to move the peroxo polyanions from the aqueous phase into the organic phase. Commonly, POM aggregates containing quaternary ammonium cations with C_8 – C_{18} alkyl groups as phase-transfer agents are used to facilitate organic phase solubility of the POM oxidant. Recently, we have reported cyclophosphazenes are also effective peroxo POM carriers between the phases.⁵ However, while we and others have had some success, more efficient biphasic oxidation processes using the POM/ H_2O_2 system could address specific challenges which include improving catalyst activity and recyclability in alkane-water

two-phase systems. This is particularly important for reactions such as the POM-catalyzed oxidative desulfurization with aqueous hydrogen peroxide as the “green” oxidant, which has been developed as a promising method for deep desulfurization of transportation fuel.^{3c} Here we show that the activity and recyclability of POM catalyst in such reactions may be improved by using functionalized alkene oligomers with much longer-chain alkyl groups as organic solvent supports as compared to the conventional phase-transfer agents.

Terminally functionalized polyisobutylene (PIB) derivatives readily soluble in nonpolar solvents like heptane have been demonstrated to have the potential to improve the recovery and recycling of homogeneous catalysts.^{6,7} These derivatives can be synthesized by functionalization of vinyl terminated PIB oligomers with a molecular weight, M_n , of 1000–2300 Da, which are commercially available.^{8,9} We now report on the use of amine terminated PIB oligomer as a highly efficient hydrocarbon solubilizing agent for Keggin POM catalysts in oxidative desulfurization and alkene epoxidation with hydrogen peroxide in a heptane-water two-phase system.

Either the oxidation of dibenzothiophene (DBT) or epoxidation of cyclooctene could be carried out in a two-phase system containing heptane as an organic solvent and aqueous H_2O_2 at 25–60 °C in a 50-mL glass reactor equipped with a magnetic stirrer, a reflux condenser and a heat circulator (see ESI†). The reactions were monitored by taking aliquots from the organic phase and submitting them to GC analysis to determine substrate conversion and product yield. After reaction, the amount of remaining H_2O_2 was determined by titration with $KMnO_4$ for the efficiency of hydrogen peroxide use to be estimated. Diethylamine terminated PIB_{1000} ($PIB_{1000}-CH_2N(CH_2CH_3)_2$) and its quaternary salt ($PIB_{1000}-CH_2N(CH_2CH_3)_2CH_3^+T$) were synthesized from commercially available⁹ PIB_{1000} by a sequence using ozonolysis, a haloform reaction, amidation, reduction, and alkylation with CH_3I (see ESI†).

The oxidation of DBT (eqn (1)) is typically employed as a model reaction for catalyst testing in oxidative desulfurization.³ We found that PIB oligomer-bound Keggin POMs are highly active and easily recyclable catalysts for DBT oxidation with H_2O_2 in a heptane-water biphasic system, yielding DBT sulfone as the sole product. The two catalyst components can simply be added separately to the reaction mixture to form the active catalyst *in situ* (eqn (2)–(3)). The PIB

amine support was introduced as a 0.5 M heptane solution of diethylamine terminated PIB. The POM was an off-the-shelf heteropoly acid hydrate $H_3PW_{12}O_{40}$, $H_3PMo_{12}O_{40}$ or $H_4SiW_{12}O_{40}$, containing roughly 20 H_2O molecules per Keggin unit, hereafter abbreviated as PW, PMo and SiW.

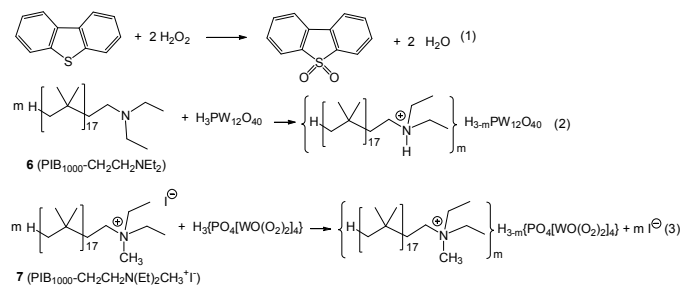


Table 1 Oxidation of DBT by H_2O_2 in heptane- H_2O two-phase system in the presence of PIB-bound POM catalysts.^a

Entry	POM	PIB/POM (mol/mol)	Temp. (°C)	Conv. (%)	H_2O_2 efficiency (%)
1	PW	1:1	60	70	> 99
2	PW	2:1	60	96	>99
3	PW	4:1	60	97	>99
4	PW	6:1	60	100	>99
5	PW	4:1	40	49	>99
6	PW	4:1	25	30	>99
7	PMo	4:1	60	73	>99
8	SiW	4:1	60	0	>99

^a Heptane (10 mL), DBT (0.50 mmol, 1 wt%), aqueous 30% H_2O_2 (0.15 mL); molar ratios: DBT/POM = 90:1, DBT/ H_2O_2 = 1:3; 0.5 h reaction time. DBT sulfone was the only reaction product observed.

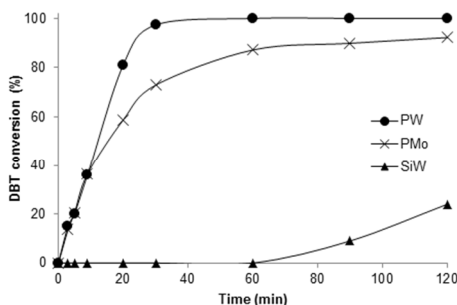


Fig. 1 Effect of POM on DBT conversion (60 °C, heptane (10 mL), DBT (0.50 mmol, 1 wt%), aqueous 30% H_2O_2 (0.15 mL); molar ratios: PIB/POM = 4:1, DBT/POM = 90:1, DBT/ H_2O_2 = 1:3).

Representative results for DBT oxidations at 25–60 °C are shown in Table 1. As expected, the catalyst activity increased with the PIB/POM molar ratio, levelling off at a ratio of 4:1 – 6:1 (entries 1–4). What is remarkable though, and different from the conventional C₈-C₁₈ quaternary ammonium surfactants, is that the catalyst was quite active already at a 1:1 PIB/POM molar ratio, giving 70% DBT conversion in 0.5 h (entry 1) and 100% in 1 h. This can be explained by the higher phase-transfer efficiency of the PIB surfactant due to its much longer hydrocarbon chain involving ca. 70 carbon atoms in total. Amongst the POMs tested, PW exhibited the highest activity followed by PMo (entries 3, 7). With PW, the conversion of DBT reached 100% in 0.5 h at 60 °C and a PIB/PW molar ratio of 6:1. In contrast, SiW showed no activity at all within 0.5 h reaction time, with a slow conversion rate after 1 h induction period (Fig. 1). This is in agreement with the well-known stability of SiW to degradation in solution^{2c} and its resistance to form peroxy species. It is important to note that practically no decomposition of H_2O_2 to molecular

oxygen took place in the PIB-POM reaction system, giving >99% efficiency of H_2O_2 utilization.

In addition to diethylamine terminated PIB oligomer, PIB₁₀₀₀-CH₂CH₂NEt₂ we also tested the corresponding quaternary salt PIB₁₀₀₀-CH₂CH₂N(Me)Et₂⁺I⁻. The latter was found to be less efficient compared to PIB₁₀₀₀-CH₂CH₂NEt₂ producing only 30% DBT conversion at 60 °C with a PIB/PW ratio of 4:1 in 0.5 h. This is not unexpected if the ion exchange in eqn (3) is less favourable than the acid base reaction in eqn (2).



Fig. 2 Catalyst recycling and phase behaviour in DBT oxidation in heptane-water two-phase system catalysed by PIB-PW (for better presentation, the amount of aqueous phase increased five-fold): (1) initial reaction system with heptane phase (top) and aqueous H_2O_2 phase (bottom); (2) the system after first reaction run complete showing DBT sulfone white precipitate; (3) the system after second extraction with acetonitrile – heptane phase (top) and acetonitrile phase (bottom); (4) the system ready for second run with fresh amounts of DBT and aqueous H_2O_2 added.

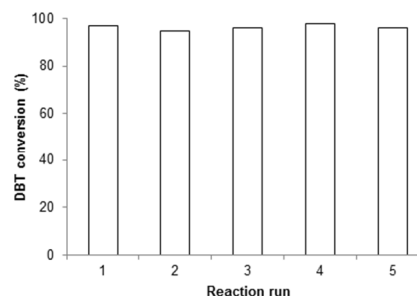


Fig. 3 Catalyst reuse in DBT oxidation (PIB-PW catalyst, 60 °C, 0.5 h, heptane (10 mL), DBT (0.50 mmol, 1 wt%), aqueous 30% H_2O_2 (0.15 mL); molar ratios: PIB/PW = 4:1, DBT/POM = 90:1, DBT/ H_2O_2 = 1:3). After each run, DBT sulfone was extracted by MeCN and fresh DBT and 30% H_2O_2 were added.

It should be pointed out that DBT sulfone is insoluble in heptane and precipitated during the reaction as a white powder. It can be quantitatively extracted from heptane-water mixture, together with water, by acetonitrile or dimethylformamide, which are immiscible with heptane.^{3b,c} On the other hand, the PIB-POM catalyst is essentially insoluble in these solvents, which allowed for easy catalyst recycling. The phase behaviour and catalyst recycling using extraction with acetonitrile is illustrated in Fig. 2. Excellent recyclability of the PIB-PW catalyst is demonstrated in Fig. 3 – the catalyst was recovered and reused five times without any loss of activity.

The catalytic performance of PIB-POM compares well with the best results reported so far. Jiang et al.^{3b} used amphiphilic decatungstate $[(CH_3)_3NC_{16}H_{33}]_4W_{10}O_{32}$ as the catalyst under similar conditions and observed similar DBT conversions (99.6%), but without giving the H_2O_2 efficiency. Similar results have also been reported for the $[(C_{18}H_{37})_2N(CH_3)_2]_3[PW_{12}O_{40}]$ catalyst.^{3c} These catalysts, however, have to be pre-synthesized via quite a laborious procedure,^{3b} which is not required for the PIB-POM system.

The PIB-POM catalyst was also found effective for the epoxidation of cyclooctene (eqn (4)) in heptane-water two-phase system. This reaction is the standard test for epoxidation catalysts and was used here for proof of concept.⁴ Usually, POM-catalyzed olefin epoxidation by H₂O₂ is carried out in homogeneous or biphasic systems using more toxic organic solvents such as acetonitrile, aromatics and chlorinated hydrocarbons.⁴ Therefore, the PIB-POM catalyst has important advantage in process safety.

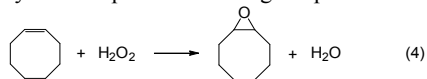


Table 2 Epoxidation of cyclooctene by 10% H₂O₂ catalyzed by PIB-POM in heptane-H₂O two-phase system.^a

Entry	POM	Temp. (°C)	PIB/POM (mol/mol)	Time (h)	Yield ^b (%)	Initial rate ^c (mmol/min)
1	PMo	60	6:1	0.5	99	0.059
2	PW	60	6:1	0.5	100	0.083
3	PW	60	5:1	0.5	97	0.085
4	PW	60	4:1	0.5	92	0.075
5	PW	60	3:1	0.5	96	0.080
6	PW	30	3:1	2.5	94	0.031
7	PW	60	2:1	0.5	92	0.065
8	PW	60	1:1	0.5	88	0.056

^aHeptane (10 mL), cyclooctene (9.71 mmol, 1.0 mL), aqueous 10% H₂O₂ (1 mmol, 0.3 mL), H₃PW₁₂O₄₀·20H₂O or H₃PMo₁₂O₄₀·28H₂O (6.48 μmol). ^bYield based on the initial amount of H₂O₂. ^cInitial rate calculated over the first 10 min of the reaction.

The oxidation of cyclooctene was carried out at 30–60 °C using 10% H₂O₂ as the oxidant and PIB-bound PW and PMo as the catalyst at a PIB/POM molar ratio of 1:1 – 6:1 (Table 2). As can be seen from the initial reaction rates, the PW catalyst was more active than PMo (entries 1 and 2), as in the case of DBT oxidation (Table 1). It was efficient already at 30 °C, yielding 94% epoxycyclooctane within 2.5 h (entry 6) and 100% at 60 °C in 0.5 h reaction time. Again, the decomposition of H₂O₂ was negligible (>99% efficiency of H₂O₂ utilization), and the catalyst could be reused. The PIB salt, PIB₁₀₀₀-CH₂CH₂N(Me)Et₂⁺T⁻, was found to be less efficient than the PIB amine, PIB₁₀₀₀-CH₂CH₂NEt₂, giving only 18% epoxide yield (60 °C, 1.5 h, PIB/PW = 6:1).

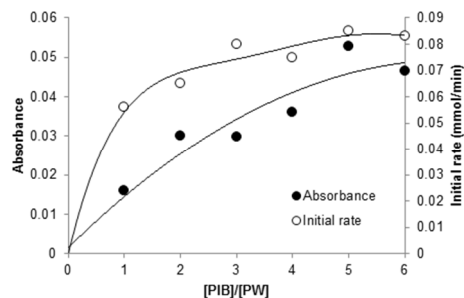


Fig. 4 Absorbance of PIB-bound PW in heptane phase at 275 nm and initial rate of cyclooctene epoxidation catalysed by PIB-PW in heptane-H₂O system (Table 2) as a function of PIB/PW molar ratio.

As in DBT oxidation, the catalyst activity decreased with decreasing the PIB/PW molar ratio due to decreasing PW transfer from aqueous to heptane phase thereupon. The PW phase transfer was estimated separately in the PW-PIB-heptane-H₂O system using UV-Vis spectroscopy by monitoring the PW charge transfer band at 275 nm at different PIB/PW molar ratios (see ESI†). Fig. 4 shows the amount of PW transferred into the heptane phase (as the UV absorption at 275 nm) and the initial rate of cyclooctene epoxidation as a function of the PIB/PW ratio. It can be seen clearly that both the

absorption and the initial rate change in parallel with the PIB/PW ratio.

The PIB-PW catalyst can be compared favourably with one of the best POM epoxidation catalysts – the lacunary silicotungstate (nBu₄N)₄[γ-SiW₁₀O₃₄(H₂O)₂] reported by Kamata et al.^{4c} This catalyst epoxidizes cyclooctene with 30% H₂O₂ in homogeneous MeCN solution at 32 °C and otherwise similar conditions, giving also 99% epoxide yield with >99% H₂O₂ efficiency. But in contrast to the straightforward preparation of PIB-POM, the synthesis of lacunary silicotungstate is an elaborate procedure.

In conclusion, we have demonstrated that the PIB oligomer-bound Keggin polyoxometalates are efficient and recyclable catalysts for environmentally benign biphasic oxidations with hydrogen peroxide, including the oxidation of DBT to DBT sulfone and cyclooctene epoxidation, in a heptane-water two-phase system. These catalysts self-assemble in situ by mixing commercial Keggin POMs and amine terminated PIB oligomer. The oxidation reactions occur through facile phase transfer of peroxy POM intermediates into the heptane phase facilitated by the amine terminated heptane phase selectively soluble PIB oligomer.

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Notes and references

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†Electronic Supplementary Information (ESI) available: Chemicals, experimental details and characterization data. See DOI: 10.1039/c000000x/

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Polyisobutylene oligomer-bound polyoxometalates as efficient and recyclable catalysts for biphasic oxidations with hydrogen peroxide

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Oxidative desulfurization and alkene epoxidation proceed in heptane-water biphasic system through facile phase transfer of POM by amine terminated oligomer.

