Tetrahedron 75 (2019) 130605

Contents lists available at ScienceDirect

Tetrahedron

journal homepage: www.elsevier.com/locate/tet

Water-soluble polymer anchored peroxotitanates as environmentally clean and recyclable catalysts for mild and selective oxidation of sulfides with H_2O_2 in water

Kabirun Ahmed, Gangutri Saikia, Sivangi Paul, Satyajit Dey Baruah, Hiya Talukdar, Mitu Sharma, Nashreen S. Islam^{*}

Department of Chemical Sciences, Tezpur University, Tezpur 784028, Assam, India

ARTICLE INFO

Article history: Received 18 July 2019 Received in revised form 5 September 2019 Accepted 11 September 2019 Available online 17 September 2019

Keywords: Peroxotitanium(IV) complexes Polymer anchored complexes Selective sulfide oxidation Aqueous reaction Homogeneous catalyst

ABSTRACT

Anchoring of peroxotitanium (pTi) species to linear water-soluble acrylic acid based polymers, poly(sodium acrylate) (PA) and poly(sodium methacrylate) (PMA) led to the successful synthesis of a pair of new, water-tolerant and recyclable catalysts of the type $[Ti_2(O_2)_2O_2(OH)_2]^{4-}$ —L (L = PA or PMA), highly effective in chemoselective sulfoxidation of organic sulfides with 30% H₂O₂ in aqueous medium at ambient temperature. The catalytic protocol is high yielding (TOF up to 11,280 h⁻¹), operationally simple as well as environmentally clean and safe, being free from halide, or any other toxic auxiliaries. The catalysts are sufficiently stable to afford easy recyclability for at least 10 consecutive reaction cycles of sulfoxidation with consistent activity selectivity profile. Oxidation of dibenzothiophene (DBT) to respective high purity sulfoxide or sulfone could also be accomplished using the same catalysts by variation of reaction conditions.

© 2019 Elsevier Ltd. All rights reserved.

1. Introduction

Water soluble peroxotitanates have been for the past several years object of intense investigation for a variety of reasons including their utility as ideal environmentally benign precursors for preparation of titanium-containing functional materials by water-based synthesis methods [1]. Most importantly, Ti(IV)–per-oxo systems have proved to be excellent and versatile oxidation catalysts, as elegantly exemplified in a wide range of oxygen transfer processes such as asymmetric epoxidation [2–8], phenol hydroxylation [3–11], ammoximation of ketone [9,12–14], transformation of sulfides to chiral sulfoxides [15–20] etc.

Chemoselective oxidation of organo sulfur compounds has been recognized as a pivotal reaction in organic chemistry, with extensive application in diverse areas ranging from desulfurization of fuel to facile synthesis of sulfoxides and sulfones [21–35]. Versatility and importance of sulfoxides and sulfones as intermediates in the synthesis of chemically and biologically important compounds

including drugs, agrochemicals and chiral auxiliaries has been extensively reported in the literature [24–33].

It has been the pioneering work of Kagan [36,37] and Modena [38], which showed the use of titanium(IV) isopropoxidediethyltartrate catalyst systems, also known as "modified Katsuki-Sharpless reagents" for asymmetric oxidation of prochiral sulfides by alkylhydroperoxides [15]. However, as the growing ecological concerns triggered an uninterrupted exploration of alternative non-polluting and sustainable oxidation protocols in recent years, aqueous H₂O₂ has emerged as an ideal clean, ecologically acceptable cost effective oxidant among the plethora of traditional oxidants available for organic oxidations [39-43]. Numerous innovative and promising transition metal homogeneous and heterogeneous catalysts with metals like vanadium [44-48], molybdenum [49–55], Iron [56–62], manganese [63–65] etc. have been reported for sulfide oxidation with H₂O₂ as terminal oxidant. A large number of catalytic systems based on well characterized salen-titanium complexes [66,67], Ti(IV) compounds with polydentate Schiff bases [68,69], other highly active systems bearing tetradentate ligands such as trialanolamine [70] and triphenolamine [71] have been developed and used as homogeneous catalysts for the oxidation of sulfides to the corresponding sulfoxides. Recently, Postigo al. have reported et







^{*} Corresponding author. Dept. of Chemical Sciences, Tezpur University, Napaam, Tezpur 784028, Assam, India.

E-mail addresses: nsi@tezu.ernet.in, nashreen.islam@rediffmail.com (N.S. Islam).

cyclopentadienyl–silsesquioxane titanium complex as a highly active catalyst for the selective oxidation of sulfide to sulfoxide and sulfone in reactions conducted in MeOH as solvent [72]. In fact, as revealed by a survey of literature, majority of existing procedures still rely upon the use of hazardous and volatile organic solvents as reaction medium [17,68,71–79] due to which the important criterion of environmental sustainability remains a challenging issue to address. Difficulty in catalyst regeneration is another limitation with respect to many of the otherwise efficient catalytic sulfoxidations, particularly in case of homogeneous systems [69,73,74,80–82]. It is notable in this context that, we have come across only few reports dealing with titanium based catalytic oxidation of sulfide that have used water as reaction medium [83–85].

Water has already been widely recognized as a natural solvent with obvious benefits of cost efficiency, nontoxicity, nonflammability, abundance and environmental compatibility, of vital importance for organic synthesis [86-95]. Apart from reducing the environmental impact, use of water as a reaction medium often facilitates simple separation and quantitative recovery of a water soluble catalyst through easy phase separation due to poor solubility of organic products in water [94,95]. A variety of commerincluding hydroformylation, cially important processes, carbonylation, hydrogenation, olefin metathe-sis, polymerization etc. have already been carried out in aqueous medium at industrial scale [91–93]. The recent upsurge in activity in the area of watercentered organic synthesis has stimulated a concomitant rise in the demand for water-tolerant and water compatible catalysts to support aqueous phase organic reactions [86,95].

Our group has previously developed a number of polymer supported heterogeneous as well as homogeneous catalysts employing peroxo derivatives of d⁰ transition metals *viz.*, vanadium [45,96–98], Niobium [99], molybdenum [49–51,100,101] and tungsten [101–104], which displayed excellent activity in a variety of organic oxidative transformations. Recently, we have reported the remarkable performance of a set of peroxo compounds of molybdenum [51], immobilized on linear water soluble polymers (WSP) viz., poly(sodium acrylate) (PA) and poly(sodium vinyl sulfonate) (PS) as highly efficient water-tolerant recyclable catalysts to achieve H₂O₂ induced sulfoxidation in aqueous medium. It is somewhat surprising that the idea of using linear WSP as support to generate catalytically active metal complexes appears to have received scant attention, although Merrifiled and Letsinger utilized soluble polymers during their pioneering work on peptide synthesis [105-107], which paved the way towards preparing immobilized homogeneous catalysts [108,109].

Encouraged by the afore mentioned observations in the present study, we focused on developing convenient, non-toxic and stable peroxotitanium compounds that can be used as environmentally safe, water-compatible recyclable catalysts to accomplish organic oxidation in aqueous medium. Titanium has been considered a good choice for our study because it is cheap, naturally abundant and non-toxic [15]. Significantly, majority of the Ti mediated sulfoxidation reactions have been achieved *via* in situ generated peroxotitanium species in the employing Ti complexes as pre-catalysts or under "Ligand Assisted Catalysis" (LAC) [35,75]. There is a paucity of information on activity of well-defined synthetic peroxotitanium complexes (**PTC**) in sulfide oxidation [76,83].

We describe herein the preparation and characterization of a pair of peroxo-Ti(IV) compounds anchored to water soluble polymer matrices, poly(sodium acrylate) (PA) and poly(sodium methacrylate) (PMA) and their activity in controlled oxidation of sulfides with H₂O₂, with respect to selectivity, TOF, reusability and ecocompatibility. The polymers, PA and PMA were chosen for the purpose of this study mainly owing to their chemical stability, ready availability and in particular, due to the presence of pendant carboxylate groups in the polymer matrices which are capable of forming facile attachment with the Ti(IV) centers. To the best of our knowledge, this is the first report dealing with synthesis of well defined pTi complexes in macroligand environment comprising of poly(acrylate) based WSP and their application as catalysts for organic oxidations.

2. Experimental section

2.1. Materials

Titanium(IV) chloride solution, 0.09 M in 20% HCl, poly(sodium acrylate) (Mw = 2100), poly(sodium methacrylate) (Mw = 4000), methyl phenyl sulfide (MPS), methyl p-tolyl sulfide (MpTS), ethyl phenyl sulfide (EPS), dimethyl sulfide (DMS), dibutyl sulfide (DBS), 2-(phenylthio)ethanol (PTE), dihexyl sulfide (DHS), diphenyl sulfide (DPS) and allyl phenyl sulfide (APS), dibenzothiophene (DBT) were purchased from Sigma–Aldrich Chemical Company, Milwaukee, USA. Acetone, methanol, ethylacetate, hydrogen peroxide, petroleum ether, silica gel (60-120 mesh), sodium hydroxide (RANKEM), diethyl ether, sodium sulfate (E. Merck, India). The water used for solution preparation was deionized and distilled.

2.2. Synthesis of water soluble peroxotitanium complexes, [Ti₂(O₂)₂O₂(OH)₂(carboxylate)]-PA (PATi) or [Ti₂(O₂)₂O₂(OH)₂(carboxylate)]-PMA (PMATi)

TiCl₄ (1.72 mL, 10 mmol) in 20% HCl solution was placed in a 100 mL beaker maintaining temperature below 4 °C in an ice bath. To this, 8 M NaOH solution was added dropwise with stirring until no further precipitation occurred. The titanic acid thus obtained was filtered and washed repeatedly with water to remove chloride as well as excess NaOH. The absence of chloride in the filtrate was confirmed by silver nitrate test. To the obtained precipitate, 30% H₂O₂ (2.26 mL, 20 mmol) was added dropwise with constant stirring until a clear yellow solution was obtained. The pH of the solution was ca. 2. To this yellowish solution, 1 g (for PATi) or 2 g (for **PMATi**) of the soluble polymer was then added in portions with continuous stirring. The pH of the system was recorded to be ca. 4 at this stage. The resulting solution was allowed to stand in an ice bath for 12 h. Subsequently, 50 mL of acetone was added to the mixture under stirring and the system was kept as such for another 2 h below 4°C. A pasty mass separated out on adding pre-cooled acetone to this mixture under vigorous stirring. The supernatant liquid was decanted off and pale yellow residue was treated repeatedly with acetone under scratching. The microcrystalline product obtained was separated by centrifugation and dried in vacuo over concentrated sulfuric acid.

2.3. Elemental analysis

For the compounds **PATi** and **PMATi**, the C and H elemental analyses were performed on an elemental analyzer (Perkin-Elmer 2400 series II). The content of titanium in the compounds was estimated with inductively coupled plasma optical emission spectrophotometer (ICP-OES) and atomic absorption spectroscopy (AAS). The weight percentage of the elements Ti, C and Na present in the compounds were also obtained from the EDX analysis. Peroxide content of the compounds was estimated by adding a weighted amount of the **PATi** or **PMATi** to a cold solution of 1.5% boric acid(w/v) in 0.7 M H₂SO₄ (100 mL). The whole system was then titrated with a standard solution of cerium(IV) [110].

2.4. Physical and spectroscopic measurements

The titanium content in the complexes were determined by inductively coupled plasma optical emission spectrophotometeric analysis (ICP-OES), using a Perkin Elmer, OPTIMA 2100 DV ICP system and atomic absorption spectroscopy (AAS) using Thermo iCE 3000 series atomic absorption spectrophotometer (model analvst 200). The IR spectra were recorded by making pressed pellets of samples with KBr using Perkin-Elmer spectrum 100 FTIR spectrophotometer. The Raman spectrums were obtained by EZRaman-N (Enwave optronics) that was equipped with a diode laser with an excitation wavelength of 785 nm and laser maximum output power of 350 mW. The measurement parameters were 10s exposure time, 5 accumulation, laser power 10% of output power and $100 \times$ objective and the pixel resolution was set to 1.44 cm^{-1} per pixel. Thermogravimetric analysis (TGA) of the compounds were performed on a SHIMADZU TGA-50 system at a heating rate of 10 °C $\rm min^{-1}$ under $\rm N_2$ atmosphere using an aluminium pan. The Energy dispersive X-ray (EDX) and Scanning electron microscopy (SEM) analysis of peroxotitanium complexes were obtained using a JEOL JSM-6390LV Scanning Electron Micrograph attached with an energy-dispersive X-ray detector. Scanning was done in the 1-20 µM range and images were taken at a magnification of 15-20 kV. The ¹³C NMR spectra were recorded on a JEOL JNM-ECS400 spectrometer at a carbon frequency of 100.5 MHz, 131072X-resolution points, number of scans 8000, 1.04 s acquisition time and 2.0 s relaxation delay with the ¹H NMR decoupling method in D₂O. The Melting points of the products were determined in open capillary tubes on a Büchi Melting Point B-540 apparatus and are uncorrected. The GC analysis was done using a CIC model 2010 gas chromatograph and an SE-52 packed column (length 2 m, 1/8 inch OD) with a flame ionization detector (FID) and nitrogen as the carrier gas (30 mL min⁻¹). The magnetic susceptibilities measurements were performed by Gouy method, using Hg [Co(NCS)] as the calibrant.

2.5. General procedure for catalytic oxidation of sulfides to sulfoxides

In a typical procedure, the sulfide oxidation reaction was carried out by placing organic substrate (5 mmol), catalyst containing 0.005 mmol of Ti [PATi (1.40 mg) or PMATi (1.88 mg)], 30% H₂O₂ (2.26 mL, 20 mmol) in 5 mL of water in a round bottom flask. The molar ratio of Ti: substrate was maintained at 1:1000 and substrate: H₂O₂ at 1:4. Reaction was conducted at ambient temperature under magnetic stirring. The progress of the reaction was monitored by thin layer chromatography (TLC) and GC. After completion of the reaction, the oxidized product along with unreacted organic substrate were extracted with diethyl ether, dried over anhydrous sodium sulfate and distilled under reduced pressure to remove excess diethyl ether. The product was then purified by column chromatography on silica gel with ethyl acetatehexane (1: 9 v/v) as the eluent. The product obtained was characterized by IR, ¹H NMR, ¹³C NMR spectroscopy and melting point determination (for solid products) [Text S1 (Supporting Information)].

2.6. General procedure for catalytic oxidation of sulfides to sulfones

To a stirred solution of 5 mmol sulfide in 5 mL water, 0.01 mmol of Ti containing catalyst [**PATi** (2.81 mg) or **PMATi** (3.77 mg)] was added, followed by addition of 50% H_2O_2 (1.36 mL, 20 mmol) in a round bottom flask. The Ti: substrate molar ratio was maintained at 1 : 500 and the substrate: H_2O_2 molar ratio at 1 : 4. The reaction was conducted at 80 °C temperature. The reaction was monitored by

thin-layer chromatography (TLC) and GC. After completion of the reaction, the system was allowed to cool to room temperature. The sulfone obtained was then isolated, purified and characterized by following similar procedure as mentioned under above section.

2.7. Regeneration of the catalyst

The recyclability of the catalyst was tested employing methyl phenyl sulfide (MPS) as the model substrate. After completion of the reaction (15 min), the product and the unreacted substrates were extracted by diethyl ether. To this spent reaction mixture, fresh batch of MPS (5 mmol) was added followed by addition of 30% hydrogen peroxide (2.26 mL, 20 mmol). The progress of the reaction was monitored by thin layer chromatography (TLC) as well as by GC and the process was repeated under optimized reaction condition (Table 4, entry 5) for minimum of ten reaction cycles. The regenerated catalyst could also be recovered as solid by adding precooled acetone to the spent reaction mixture that was kept on an ice bath after the completion of the reaction and extraction of the product.

2.8. Computational details

In the present work, we have performed all the computation as in Dmol³ program package [111,112]. Local Density Approximation (LDA) [113] using (PWC) functional has been used to optimize the electronic structures of the complexes with double numerical with polarization (DNP) [114,115] basis set for our calculations. DNP basis set used for our calculations is comparable to Gaussian 6-31G**, but DNP is more accurate than a Gaussian basis set of the same size [116,117]. For the vibrational frequency calculations, same level of theory was used. We have obtained stable minima which correspond to the real and positive values. To improve computational performance, a global orbital cutoff of 4.5 Å was employed. Self-consistent field (SCF) procedures are done with tolerances of the energy, gradient, and displacement convergences: 1.0×10^{-5} Ha, 2×10^{-3} Ha Å, and 5×10^{-3} Å, respectively.

3. Results and discussion

3.1. Synthesis and characterization

The synthesis of water soluble macromolecular peroxotitanium complexes PATi and PMATi were achieved by reacting freshly prepared titanic acid with 30% H₂O₂ in presence of the respective carboxylate containing WSP, poly(sodium acrylate) (PA) or poly(sodium methacrylate) (PMA). Titanic acid was obtained by employing a procedure introduced by Kakihana et al. [1], based on the reaction of TiCl₄ in 20% HCl with NaOH. The maintenance of pH of *ca*. 4 was found to be crucial for the formation of the u-oxo peroxoTi(IV) complexes and their co-ordination to the pendant carboxylate groups of the polymer chain. The peroxo-hydroxo titanium complexes formed in an acidic solution have been known to undergo facile dimerization to afford stable oxo-bridged di-titanium complexes with Ti₂O₂ core [118–122]. Ligands possessing carboxylate groups have been reported to stabilize peroxotitanium species, leading to the development of a host of highly stable peroxotitanium complexes with carboxylate containing co-ligands [123–126]. One of the advantages of using water soluble polymeric ligands, which are essentially polychelatogens, is the convenience of adopting synthetic procedures used for obtaining their monomeric analogues. The immobilized catalysts PATi and PMATi, finally obtained as solids by solvent induced precipitation, remain stable and can be stored dry at ambient temperature for several weeks.

The elemental analysis data of the catalysts revealed the ratio of $Ti:O_2^{2-}$ content to be unity, showing that the anchored **pTi** moieties occur in the catalysts in their monoperoxo configuration. The titanium loading on the polymer matrices, calculated from the Ti content of the catalysts was observed to be higher than that of the Mo containing analogues synthesized previously by us [Table S1 (Supporting Information)] [51,100]. The metal: ligand ratio for the catalysts **PMATi** and **PATi** was found to be 1:2 and 1:1.5, respectively. Magnetic susceptibility measurements revealed the diamagnetic nature of the compounds, testifying to the occurrence of Ti in its +4 oxidation state in each of them.

3.1.1. SEM and energy dispersive X-ray (EDX) analysis

The scanning electron micrographs of the polymer anchored complexes showed noticeable alteration of their surfaces in comparison to the even surfaces of the pure polymers (Fig. 1a and c). That the metal ions are distributed across the surface of the polymer was evident from the morphological changes occurring on the polymers after metal incorporation. (Fig. 1b and d).

From the energy dispersive X-ray (EDX) spectroscopic analysis, carried out by focusing regions over the surface of the compounds, it was further confirmed that Ti, C, O, Na are the constituents of the catalysts (Fig. 2). The EDX analysis data obtained on the composition of the compounds were in good agreement with the elemental analysis values [Table S1 (Supporting Information)].

3.1.2. FTIR and Raman spectral studies

Raman and IR spectra of each of the compounds displayed typical absorption in the vicinity of *ca*. 860 cm⁻¹ attributable to v(O-O) mode of coordinated peroxo group, in addition to the complementary $v_{asym}(Ti-O_2)$ and $v_{sym}(Ti-O_2)$ modes, as has been

expected, in the 500-600 cm⁻¹ region [118,127–138]. The IR spectra of **PMATi** and **PATi** are presented in Fig. 3 and Fig. S1 (Supporting Information), respectively, and the corresponding Raman spectra are shown in Fig. 4.

The significant IR and Raman spectral data for the compounds are summarized in Table 1. The weak intensity band observed in the 750-780 cm⁻¹ region in the IR spectra has been assigned to Ti–O–Ti stretching vibration of μ -oxotitanium dimer [83,121,135,137]. The corresponding absorption appeared as a sharp band in the Raman spectra of the compounds at ca. 790 cm⁻¹. The Ti–OH bending mode corresponding to the terminal –OH groups of the complexes manifested at 1104 cm⁻¹ in **PATi** and at 1120 cm⁻¹ in **PMATi**, corresponding to Raman band at *ca*. 1109 and 1138 cm,⁻¹ respectively [128,131,136]. The ν (OH) modes appeared as a broad band in the spectrum of each of the complexes in the 3300-3500 cm⁻¹ [127–138].

The intense band observed in the IR spectrum of the poly(acrylate) bound complex, **PATi** at 1626 cm⁻¹ and a weak absorption occurring at 1391 cm⁻¹ have been ascribed to v_{asym} and v_{sym} stretching vibrations, respectively of deprotonated and coordinated carboxyl groups [139,140]. The corresponding bands in the poly(methacrylate) anchored compound **PMATi** were observed at 1647 and 1407 cm⁻¹, respectively. The observed shift of v_{asym} (-COO) to a higher frequency and that of v_{sym} (COO) to a lower frequency in the complexes relative to the free polymer values (Table 1), resulting in the magnitude of wavenumber difference of *ca*. 230 cm⁻¹, provided clear indication of unidentate co-ordination of COO⁻ groups in each of the compounds [51,99,139,140]. The IR and Raman spectra also indicated the presence of free –COOH in the compounds showing absorptions at *ca*. 1710 cm⁻¹ [139,140].



Fig. 1. Scanning electron micrographs of (a) PMA, (b) PMATi, (c) PA and (d) PATi.



Fig. 2. EDX spectrum (2a, 2c) PMATi and (2b, 2d) PATi.

3.1.3. Electronic spectral studies

The electronic spectra of the complexes **PATi** and **PMATi**, recorded in H₂O showed a well resolved broad band at 350–360 nm region, in addition to a sharp and intense absorption at 215 nm [Fig. S2 (Supporting Information)]. In line with the previous literature on peroxotitanium(IV) complexes [125,127,141], the weaker band at 350–360 nm could be attributed to π_v *êd peroxo to metal charge transfer (LMCT) transition, whereas the intense peak appearing at higher energy at 215 nm has been assigned to π_h *êd σ * LMCT transition.

3.1.4. ¹³C NMR studies

The ¹³C NMR spectra of the catalysts and the respective pristine polymers, **PA** and **PMA** are presented in Fig. 5. The spectral pattern along with the corresponding chemical shift data listed in Table 2, provided complementary information indicating modification of carbon resonances of the polymer support to varying degrees after anchoring of Ti(IV) species.

The major resonances have been assigned on the basis of available literature [142–151]. The spectra of the free polymers **PA** and **PMA** showed carboxylate carbon resonances at lower end of the field at 187 and 184 ppm, respectively [142–145], apart from the expected signals corresponding to the chain carbon atoms. The spectra of the Ti anchored macro complexes on the other hand

displayed an additional peak at much lower field of *ca*. 215 ppm which may be ascribed to the C atom of the metal coordinated carboxylate group. The observed large downfield shift, $\Delta\delta$ ($\delta_{complex}$ - $\delta_{free\ carboxylate}$) of 28 ppm in **PMATi** and 31 ppm in **PATi** suggested presence of strong metal ligand interactions in the macromolecular complexes, as has been reported earlier [49,99,100,140].

3.1.5. TGA-DTG analysis

The TGA-DTG profile of the complexes (Fig. 6) show multistage of degradation with major break down processes that reveal the compound compositions and phase transition in each of the complexes [Table S2 (Supporting information)]. The first step of weight loss due to the liberation of physisorbed water molecules from the catalysts occurred between room temperature and ca.108 °C. The second degradation stage in the temperature range of 170-303 °C in PMATi and 166-220 °C in PATi is attributable to the decomposition and loss of co-ordinated peroxo groups of peroxotitanium moieties anchored to the polymer [129,152–155]. The absence of peroxide group in the decomposition product, isolated at this stage, was also verified by its IR spectrum. The subsequent step occurred between the range of 221–280 °C in PATi with a weight loss of 6.5% which may be ascribed to the decomposition of terminal -OH group by analogy with previous reports on some dimeric hydroxoperoxo Ti(IV) complexes possessing terminal Ti-OH group



Fig. 3. IR spectrum of (a) pristine polymer PMA, (b) original catalyst PMATi and (c) catalyst PMATi regenerated after 10th reaction cycle in water.

[128,131,155]. The observed weight loss is in good agreement with the value of 6.4% calculated for the compound PATi. The corresponding degradation step in the compound **PMATi** was observed at a relatively higher temperature range of 329-388 °C with a weight loss of 5.6% which is close to the calculated value of 5.55%. On increasing the temperature further, degradations attributable to decarboxylation of carboxylate functional groups accompanied by rupture of polymers chain occurs in the broad temperature range of 394–538 °C for **PMATi** and for **PATi**, in the temperature range of 359 °C upto 520 °C, respectively [100,140]. The residue remaining after the complete degradation of the polymer immobilized compounds was found to be oxotitanium species. This was further confirmed from the IR spectra recorded after heating the compounds separately up to the final decomposition temperature which revealed complete disappearance of absorptions attributable to peroxo and terminal Ti–OH stretching as well as the strong peaks originating from v(COO) of the original compounds. Thus the TGA- DTG analysis data furnished additional evidence in support of the composition and formula assigned to the macrocomplexes.

3.1.6. Density functional studies

We have carried out theoretical investigations employing the density functional theory (DFT) method with an aim to examine the feasibility of structures proposed for the polymer anchored pTi catalysts. In line with our previous work on some other polymer supported peroxometallates [55,99,100], a model complex has been generated corresponding to a section of the poly(acrylate) anchored pTi catalyst PATi (Fig. 7), on the basis of experimentally derived structural information (FTIR, Raman, ¹³C NMR, TGA, EDX and elemental analysis). DFT calculations were performed on the



Fig. 4. Raman spectrum of (a) PMATi and (b) PATi.

 Table 1

 Infrared (IR) and Raman(R) spectral data (cm^{-1}) for PMATi and PATi compounds.^a

Assignment		PMA	PMATi	PA	PATi
v _{asym} (COO)	(IR)	1540(s)	1701(s), 1647(br,s)	1565(s)	1710(s),
	(R)	-	1708(m),	-	1626(br,s)
			1643(m)		1710(m),
					1592(w)
$v_{sym}(COO)$	(IR)	1415(s)	1407(w)	1409(s)	1391(w)
	(R)	-	1405(m)		1347(s)
ν(O-O)	(IR)	_	848(s)	_	863(s)
	(R)		839(vs)		879(vs)
$v_{sym}(Ti-O_2)$	(IR)	_	531(m)	_	525(m)
	(R)		523(s)		527(m)
$v_{asym}(Ti-O_2)$	(IR)	_	614(m)	_	619(w)
	(R)		607(s)		613(m)
$\nu(Ti-OH)$	(IR)	_	1120(m)	_	1104(s)
	(R)		1138(m)		1109(s)
$\nu(Ti-O-Ti)$	(IR)	_	753(w)	_	766(w)
	(R)		815(s)		795(s)

^a vs, very strong; br, broad; s, strong; m, medium; w, weak.

model complex at PWC/DNP level of theory [113–115]. The optimized structure of the complex presented in Fig. 7 shows three repeating unit of the polymer with one dinuclear peroxotitanium(IV) complex with di- μ -oxo Ti₂O₂ core bonded to the polymer chain through its carboxylate groups. Bonding of O atom of terminal –OH group completes hexa co-ordination around each of



Fig. 5. ¹³C NMR spectrum of a) PMA b) PMATi, c) PA and d) PATi.

 Table 2

 ¹³C NMR chemical shift data for polymer-anchored peroxotitanium complexes and free polymer.

Compound	Chemical	shift (ppm)			
	Carboxyla	te carbon	СН	CH ₂	CH ₃
	Free	Complexed			
PMA PMATi	187.41 187.44	215.51		17.36 17.25	56.54 55.69
PA PATi	184.50 184.57	215.49	45.52 45.59	36.10 35.92	

Ti(IV) centers as has been observed in a majority of the reported pTi complexes. The structure also indicated participation of -OH groups in H-bond formation with neighbouring -COOH groups as well as one of the metal bound peroxo ligands. After optimization of the structure vibrational frequencies were calculated to conform to the stability of the complex. Absence of negative vibrational frequency (imaginary frequency) in the vibrational frequency calculations implied that the complex represents a stable structure. Moreover, the vibrational frequencies calculated for the optimized geometry (Table S3, supporting information) was observed to simulate well with the experimentally determined IR spectral data. The selected geometrical parameters such as bond lengths and bond angles obtained from the theoretical calculations listed in Table 3 have been found to be in good agreement with the reported crystallographic parameters corresponding to heteroleptic monoperoxotitanium complexes [122,156-159]. Thus, the mutually consistent findings of our theoretical studies and experimental results completely validate the predicted structures of the synthesized catalysts. Di- μ -oxo titanium complexes with Ti₂O₂ core have been reported in variety of ligand environment which is known to impart stability to the peroxotitanium(IV) complex species [6,118-122].



Fig. 6. TGA spectrum of (a) PMATi and (b) PATi.



Fig. 7. Optimized geometry for complex **PATI**. The numerical numbers represent the labelling of the atoms as in Table 3.

3.2. Catalytic activity of the synthesized complexes PMATi and PATi in oxidation of sulfides

3.2.1. Oxidation of sulfides to sulfoxides

In order to assess the catalytic potential of the peroxo titanium macro complexes we first examined the sulfoxidation of methyl phenyl sulfide (MPS) as a model substrate using **PMATi** as a representative catalyst with 30% H_2O_2 as oxidant. To screen the optimal reaction condition, a preliminary experiment was conducted maintaining catalyst: MPS and MPS: H_2O_2 molar ratio as 1: 500 and 1: 2, respectively. The reaction was carried out in water at ambient temperature under magnetic stirring in complete absence of organic solvent. It was gratifying to note that oxidation of thioanisole was virtually quantitative under these conditions and provided the corresponding sulfoxide with complete selectivity and a good TOF within an hour (Table 4, entry 1). We have subsequently proceeded to optimize the reaction by assessing the influence of various reaction parameters *viz.*, solvent type, catalyst concentration, oxidant: substrate stoichiometry and reaction temperature as

shown in Table 4.

We have examined the reaction under three different catalyst concentrations, in addition to conducting a blank run in absence of the catalyst, under otherwise identical reaction conditions. The role of the catalyst is very much evident when the conversions were compared to the result of the control run which provided poor conversion not exceeding 13%, under identical condition (Table 4, entry 11). From the data presented in Table 4(entries 1–3), it is noticeable that increasing the catalyst amount elevated the reaction rate considerably without affecting the sulfoxide selectivity, although no significant improvement was seen with respect to TOF at higher catalyst concentration. On the other hand, a reasonably good TOF was obtained along with sulfoxide selectivity (Table 4, entry 3) even at a low catalyst: substrate ratio of 1:2000.

Next, a concentration dependent study was carried out with respect to the oxidant: substrate stoichiometry, using three different equivalents of 30% H_2O_2 under analogous reaction conditions. As demonstrated by the data (Table 4, entries 2, 4 and 5), increasing oxidant concentration from 2 to 4 equivalents accelerated the reaction considerably, leading to nearly 5-fold enhancement of TOF with 4 equivalents of H_2O_2 . It is also notable that the sulfoxide selectivity remained unaffected and no overoxidation to sulfone occurred even at relatively higher oxidant concentration used. The above findings collectively indicated that a substrate: H_2O_2 of 1:4 with Ti: substrate molar ratio maintained at 1: 1000 was optimal to achieve best results in terms of selectivity as well as TOF.

The impressive results achieved in aqueous medium prompted us to screen the water soluble catalyst for its compatibility with some common organic solvents. Significantly, despite the insolubility of the catalysts in the neat organic solvents, both the compounds dissolved completely in water miscible organic solvents, methanol and acetonitrile in presence of aqueous H₂O₂, leading to homogeneity of the catalytic process. Pertinent here is to mention that we have avoided the use of hazardous chlorinated solvents in our present work. As seen from data in Table 4 (entries 6 and 7), the catalysts are compatible with the chosen organic solvents as well. To our pleasure however, water emerged to be the best solvent providing maximum catalyst efficiency in terms of both product selectivity as well as superior rate (Table 4, entry 5). The observation is not surprising as it has been already established by Sharpless et al. followed by others that solubility of the organic reagents is not a basic requirement for reactions to occur optimally in neat water 51,87,99].

A further striking feature of the protocol is the remarkable

Table 3

Selected bond lengths (Å) and bond angles (degree) for PATi calculated using density functional theory (DFT) as implemented in DMol³ package.

Complex PATi			
Structural index ^a	Calculated values	Structural index ^a	Calculated values
Ti1-02	1.889	Ti8–09	2.138
Ti1-03	1.988	C15-O10	1.256
02–03	1.437	∠012–Ti8–013	41.32
Ti1-06	1.854	∠Ti8–013–012	62.16
Ti1-07	1.956	∠Ti8-012-013	76.52
C21-O9	1.258	∠Ti8–011–H14	86.58
04-H5	0.985	∠Ti1-02-03	71.96
Ti1-04	1.914	∠Ti1-03-02	64.63
Ti8-012	1.916	∠02-Ti1-03	43.41
012-013	1.431	∠Ti1-04-H5	112.38
Ti8-06	1.889	∠Ti1–07–Ti8	97.12
Ti8-07	1.810	∠Ti1–O6–Ti8	97.99
Ti8-011	2.062	∠07-Ti1-06	80.95
O11-H14	0.986	∠07–Ti8–06	83.92

^a See Fig. 7 for the atomic numbering.

			Solve	PMATi	S la	+ 5 1b			
Entry	Molar ratio (Ti:MPS)	H ₂ O ₂ Equiv.	Solvent	Temperature	Time (min)	Isolated yield (%)	1a:1b	TON ^b	$TOF^{c}(h^{-1})$
1	1:500	2	H ₂ O	RT	35	94	100:0	470	806
2	1:1000	2	H ₂ O	RT	65	96	100:0	960	887
3	1:2000	2	H ₂ O	RT	150	96	100:0	1920	768
4	1:1000	3	H ₂ O	RT	40	96	100:0	960	1440
5	1:1000	4	H ₂ O	RT	15	97	100:0	970	3880
6	1:1000	4	MeOH	RT	25	98	100:0	980	2352
7	1:1000	4	CH ₃ CN	RT	35	96	100:0	960	1646
8	1:1000	2	H ₂ O	60 ° C	35	95	100:0	950	1626
9	1:2000	2	MeOH	65 °C	10	95	100:0	1900	11400
10	1:2000	4	H ₂ O	RT	75	96	100:0	1920	1536
1 1 d		4	11.0	DT	15	10	100.0		

Table 4 Optimization of reaction conditions for **PMATi** catalyzed selective oxidation of methyl phenyl sulfide to methyl phenyl sulfoxide by 30% H₂O₂^a.

^a All the reactions were carried out with 5 mmol of substrate in 5 mL of solvent. Catalyst amount = 1.8 mg for 0.005 mmol of Ti.

^b TON (turnover number) = mmol of product per mmol of catalyst.

^c TOF (turnover frequency) = mmol of product per mmol of catalyst per hour.

^d Blank experiment without any catalyst.

improvement of the rate of reaction achieved on increasing the reaction temperature from RT to $60 \,^{\circ}$ C in water and $65 \,^{\circ}$ C in methanol without affecting the selectivity. Thus the TOF could be elevated to a high value of (11400 h⁻¹) with 100% sulfoxide selectivity in refluxing methanol (Table 4, entry 9). Nevertheless, we preferred to carry out the reactions at room temperature due to the environmentally benign aspect. It has also been ascertained that neither light nor air had any observable influence on the rates of the catalytic oxidations.

Having standardized the appropriate conditions for sulfoxidation of MPS (Scheme 1), we proceeded to establish the scope of the catalysts and the developed protocol using a wide variety of substrates. The reactivity data summarized in Table 5 demonstrate that clean conversion of the chosen aliphatic or aromatic substrates to the corresponding sulfoxide occurred in presence of each of the catalysts within a reasonably short time, providing excellent yield and TOF (Table 5, entries 1-15). The catalyst PMATi displayed consistently superior activity compared to the PATi. In fact, considering the mild reaction conditions the TOF values obtained in the present study, reaching up to a highest value of 11,280 h^{-1} (Table 5, entry 2), are indeed remarkable in comparison to most of the water-based catalytic sulfoxidations reported so far [52,83-85,160-163]. Both the catalysts displayed high functional group tolerance towards sensitive groups such C=C and OH. Thus allylic and alcoholic sulfides were chemoselectively oxidized to yield targeted sulfoxide without affecting any other functional group transformation under the optimized condition.

Versatility of the developed catalysts is further evident from the fact that, a least nucleophilic and refractory sulfide like dibenzothiophene (DBT) could also be selectively oxidized to sulfoxide in presence of the catalysts by modification of reaction condition. As the DBT oxidation was too slow in water, it was advantageous to make use of the compatibility of the catalysts in organic medium to attain the intended oxidation by performing the reaction in MeOH. Although complete conversion was not achieved upto 12 h of reaction time, but the TON obtained in case of DBT oxidation was considerably higher compared to most of the other reported titanium catalyst based sulfoxidation reaction [23,35,78].

3.2.2. Oxidation of sulfides to sulfones

Subsequently, we have directed our efforts towards developing methodology to attain selective oxidation of sulfide to sulfone using the same catalysts. Our initial attempts to obtain the targeted sulfone from the model substrate, thioanisole using 30% H₂O₂ in a reaction conducted in water, was unsuccessful. However, taking cues from our past experience pertaining to sulfide oxidation with polymer supported peroxometal catalysts [49], we could finally accomplish complete conversion of MPS, to pure sulfone in aqueous medium at ambient temperature using 4 equivalents of 50% H₂O₂ (Table 6, entry 3) with catalyst: substrate molar ratio maintained at 1:500. Although the reaction was rather sluggish at room temperature, the reaction rate and hence the TOF could be substantially improved without affecting the selectivity, by increasing the reaction temperature gradually to 80 °C (Table 6, entry 6). After investigating the solvent effect on the rate of the oxidation (Table 6, entries 8 and 10), it was satisfying to note that the catalyst was most potent in water as has been observed in case of sulfoxidation reaction. In methanol and acetonitrile the catalyst displayed comparable activity at RT. In addition to thioanisole, as shown in entries 1–15 of Table 7, the developed oxidation protocol could be conveniently applied to variously substituted aromatic and aliphatic sulfides, regardless of the catalyst used. For DBT oxidation, however, we could achieve the desired results by conducting the reaction in acetonitrile at 78 °C, instead of water, using a higher



Scheme 1. Optimized reaction conditions for the selective oxidation of sulfides to sulfoxides or sulfones by pTi compounds.

Table 5

Selective oxidation of sulfides to sulfoxides catalyzed by PMATi and PATi with 30% H₂O₂ using water as solvent.^a

<u>د</u>	PMATi or PATi (Ti: S =1:1000)	
R R'	30% H ₂ O ₂ (4 equivalents), H ₂ O	R R'

~

Entry	Substrate	PMATi				PATi			
		Time (min)	Isolated yield (%)	TON ^b	$TOF^{c}(h^{-1})$	Time (min)	Isolated yield (%)	TON ^b	$TOF^{c}(h^{-1})$
1	C S	15 15	97 94 ^d	970 940	3880 3760	20 20	98 95 ^d	980 950	2940 2850
2	∕ ^S ∕	5	94	940	11280	9	97	970	6466
3	∽~s∽~	10	97	970	5820	15	94	940	3760
4	$\sim \sim _{S} \sim \sim \sim$	10	95	950	5700	17	95	950	3353
5	S_S_	15	92	920	3680	20	96	960	2880
6	S S	17	96	960	3388	25	95	950	2280
7	S	25	96	960	2304	35	95	950	1632
8	С С С С С С С С С С С С С С С С С С С	70	94	940	806	100	94	940	564
9	S_S_S	55	95	950	1036	80	96	960	720
10	SBr	65	96	960	886	80	97	970	727
11	S-CI	70	97	970	829	85	96	960	677
12	s	160	95	950	356	180	96	960	320
13	C S C	190	94	940	297	205	95	950	278
14 ^e	⟨s	175	97	970	333	200	97	970	291
15 ^f	S	12h	90	90	7.5	12h	85	85	7

^a All reactions were carried out with 5 mmol substrates, 20 mmol 30% H2O2 and catalyst (0.005 mmol of Ti) in 5 mL H2O at RT, unless otherwise indicated.

^b TON (turnover number) = mmol of product per mmol of catalyst.

^c TOF (turnover frequency) = mmol of product per mmol of catalyst per hour.

^d Yield of 10th reaction cycle.

^e Reaction condition: 5 mmol substrate, 20 mmol 30% H2O2 and catalyst (0.005 mmol of Ti) in 5 mL methanol at RT.

^f Reaction condition: 5 mmol substrate, 20 mmol 30% H₂O₂ and catalyst (0.05 mmol of Ti) at 65 °C in refluxing methanol.

amount of catalyst (substrate: catalyst = 1:100 M ratio). Most importantly, despite the presence of excess of 50% H₂O₂ and a relatively higher reaction temperature maintained, the oxidation of sulfide to sulfone proceeded with complete chemoselectivity (Table 7, entries 8 and 9) leaving the co-existing alcohol and C=C groups unaffected.

3.2.3. Recyclability of the catalysts

Stability of a catalyst and its recyclability are crucial for its practical utility in a catalytic process. The recyclability of both the catalysts were tested up to 10 reaction cycles using MPS as the model substrate in water under optimized reaction conditions. The catalysts could be recycled by adding fresh batch of oxidant and substrate to the aqueous phase of the spent reaction mixture on

Table 6

Optimization of reaction conditions for **PMATi** catalyzed oxidation of methyl phenyl sulfide to methyl phenyl sulfore by 50% H₂O₂.^a



Entry	Molar ratio (Ti:MPS)	H ₂ O ₂ Equiv.	Solvent	Temperature	Time (h)	Isolated yield (%)	1a:1b	TON ^b	$\text{TOF}^{c}(h^{-1})$
1	1:1000	2	H ₂ O	RT	10	93	77:23	930	93
2	1:500	2	H ₂ O	RT	9	94	41:59	470	52
3	1:500	4	H ₂ O	RT	7.6	98	0:100	490	64
4	1:500	4	H ₂ O	60 °C	6	96	0:100	480	80
5	1:500	4	H_2O	70 °C	4.5	98	0:100	490	108
6	1:500	4	H ₂ O	80 °C	3	98	0:100	490	163
7	1:100	4	H_2O	80 °C	1.3	97	0:100	485	72
8	1:500	4	CH ₃ CN	RT	24	94	40:60	470	19
9	1:500	4	CH ₃ CN	78 °C	9	98	0:100	490	55
10	1:500	4	MeOH	RT	24	95	55:45	475	20
11	1:500	4	MeOH	60 °C	20	99	0:100	495	25

^a All the reactions were carried out with 5 mmol of substrate in 5 mL of solvent. Catalyst amount = 3.7 mg for 0.01 mmol of Ti.

^b TON (turnover number) = mmol of product per mmol of catalyst.

^c TOF (turnover frequency) = mmol of product per mmol of catalyst per hour.

 $\begin{array}{l} \textbf{Table 7} \\ \textbf{Selective oxidation of sulfides to sulfones catalyzed by \textbf{PMATi} and \textbf{PATi} with 50\%\,H_2O_2 \text{ using water as solvent.}^a \end{array}$



Entry	Substrate	PMATi				PATi			
		Time (min)	Isolated yield (%)	TON ^b	$TOF^{c}(h^{-1})$	Time (min)	Isolated yield (%)	TON ^b	$TOF^{c}(h^{-1})$
1	S_	180	98 90 ^d	490 450	163 150	205	97 92 ^d	485 460	142 134
2	∕ ^s ∕	50	96	480	578	65	96	480	444
3	\sim s \sim	75	98	490	392	85	97	485	342
4	$\sim \sim $	80	97	485	364	85	98	490	347
5	S_	180	97	485	162	195	96	480	148
6	S_	185	98	490	159	205	97	485	142
7	S~	225	96	480	128	230	97	485	127
8	ССССОН	380	93	465	73	395	95	475	72
9	C,S∽∽	350	95	475	81	370	97	485	78
10	SBr	305	98	490	96	330	96	480	87
11	s	310	97	485	94	335	98	490	88
12	s-	440	98	490	67	465	97	485	63

(continued on next page)

Table 7 (continued)

Entry	Substrate	PMATi				PATi			
		Time (min)	Isolated yield (%)	TON ^b	$TOF^{c}(h^{-1})$	Time (min)	Isolated yield (%)	TON ^b	$TOF^{c}(h^{-1})$
13	C) ^S C)	510	94	470	55	535	96	480	53.8
14 ^e	S	480	97	485	60.6	500	96	480	58
15 ^f	S → S → S → S → S → S → S → S → S → S →	720	85	85	7	720	80	80	6.7

^a All reactions were carried out with 5 mmol substrates, 20 mmol 50% H₂O₂ and catalyst (0.01 mmol of Ti) in 5 mL H₂O at 80 °C, unless otherwise indicated.

^b TON (turnover number) = mmol of product per mmol of catalyst.

^c TOF (turnover frequency) = mmol of product per mmol of catalyst per hour.

^d Yield of 5th reaction cycle.

^e Reaction condition: 5 mmol substrate, 20 mmol 50% H₂O₂ and catalyst (0.01 mmol of Ti) in 5 mL methanol at 60 °C.

^f Reaction condition: 5 mmol substrate, 20 mmol 50% H₂O₂ and catalyst (0.05 mmol of Ti) at 78 °C in refluxing acetonitrile.

completion of each catalytic cycle. The recycling performances of the catalysts presented in Fig. 8 demonstrated the impressive reusability of the catalyst at least up to 10 catalytic cycles with consistent activity and selectivity. In order to further confirm that the catalysts remain intact during the cycles of oxidations we have also performed recycling experiments at shorter duration of the reaction by stopping the reaction after 10 min, and then conducting the subsequent reaction run [Table S4 (Supporting information)]. The results of experiments carried out up to 4th reaction cycles at shoter reaction time, showed no significant lowering in yield or selectivity of the catalysts.

We have also characterized the regenerated catalysts after isolating it as solid, by elemental and spectral analysis in order to further confirm that the catalysts remain intact during the cycles of oxidations. The FTIR and Raman spectra of the regenerated catalysts displayed the characteristic peaks that are present in the pristine catalyst [Figs. S1 and S3 (Supporting information)]. As revealed by elemental analysis and EDX data, no significant decrease in peroxide content or metal loading occurred, ruling out the possibility of metal leaching out of the polymer support during the catalytic process. Thus it has been established that the catalysts are structurally robust reflecting the strong attachment of the pTi species to the polymer chain.

The reusability of the catalysts in oxidation of sulfide to sulfone was also examined following a similar methodology. Fig. 9 shows the no. of cycles vs. % yield in the selective oxidation reaction of sulfide to sulfone. Both the catalysts showed good activity retaining the selectivity upto nearly fifth reaction cycles. However, a gradual fall in % conversion was observed in the subsequent cycles indicating possible degradation of the catalyst. This may not be unusual keeping in view the relatively higher reaction temperature maintained as well as longer reaction time required for the complete conversion of sulfides to sulfones.

A comparative report on selective oxidation of MPS by some of the reported homogeneous Ti based catalyst systems is presented in Table 8, which demonstrate the merit of the developed pTi catalysts, **PATi** and **PMATi** in terms of conversion rate, selectivity, reusability and reaction conditions employed. Although a precise comparison of the efficiency of the catalysts **PATi** and **PMATi** in terms of TON or TOF obtained with different reported examples is



Fig. 8. Recyclability of catalysts **PMATi** and **PATi** for the selective oxidation of sulfide to sulfoxide in water.



Fig. 9. Recyclability of catalysts PMATi and PATi for the oxidation of sulfide to sulfone in water.

Comparison of catalytic performance of PATi or PMATi with literature reported titanium based homogenous catalytic systems for oxidation of sulfides using H_2O_2 as oxidant

Entry	/ Catalyst	Reaction condition	Time (min)	%Conversion (% yield)/ selectivity	Recycling Run/no. of recycling	Ref.
1	РМАТі	Water, RT	15	100/100 (TOF = 3880)	Yes/10	This Work
2	PATi	Water, RT	20	100/100 (TOF = 2940)	Yes/10	
3	K ₁₆ [Ti ₂₀ (μ-O) ₈	Water, RT	90	89.4/91.6	No	[83]
	$(HO_2)_8(O_2)_{12}(R,R-tart)_{12}] \cdot 52H_2O$					
4	PN ₆₈ (IS) ₄	Water, 25 °C	60	99/95	Yes/7	[84]
5	Ti(IV) complexes bearing a chiral polydentate ligand	MeOH, RT	5	99/100	No	[69]
	based on α-pinene					
6	TOC-1	MeOH, 40 °C	15	98/99	Yes/4	[79]
7	TOC-2	MeOH, 40 °C	15	93/96	No	
8	Ti(Phen)(OC ₂ H ₅) ₂ Cl ₂	MeOH, RT	20	99/98 (TOF = 1182)	Yes/8	[75]
9	Ti(Oi-Pr) ₄ + Schiff base ligand	MeOH and water mixture, dry DCM,	90	95/94	No	[164]
		N ₂ atm, 0 °C				
10	Ti(Oi-Pr) ₄ + Shiff base	Dry dichloro methane, 0 °C	600	92/93	No	[73]
11	Ti (IV) amino triphenolate complexes	Chloroform, 28 °C	120	97/98	No	[71]
12	Ti(IV)–Isopropoxide complexes	MeOH, N ₂ atm, RT	30	90/91	No	[35]
13	Ti(IV)-Amino triphenolate complexes	MeOH, 28 °C	20	96/98	No	[81]
14	Titanium substituted heteropolytungstate	Dichloro ethane, 25 °C	90	72/86	No	[82]

^a Substrate considered is methyl phenyl sulfide(MPS).

not possible in absence of sufficient reported kinetic data, nevertheless it is evident from our findings that, pTi compounds provide benefits of both homogeneous and heterogeneous catalysts by displaying excellent activity along with good recyclability which demonstrate the synthetic value of the protocol [35,69,71,73,75,79,81–84,164,165]. These results are especially significant considering the truly mild reaction conditions under which the reactions have been accomplished using green solvent water as reaction medium at ambient temperature.

3.2.4. The proposed catalytic cycle

The mechanism of action of titanium based catalysts in H_2O_2 induced oxygen transfer processes such as sulfoxidation, epoxidation, oxidation of allylic alcohol has been extensively investigated [35,72,134,138,166–171]. It has been known to proceed by in situ activation of peroxide *via* formation of an active peroxotitanium species, in which peroxo group is usually η^2 co-ordinated to Ti(IV) [35,72,138,166–171]. Based on these observations along with findings of our present study, we propose a credible catalytic cycle for selective oxidation of sulfides to sulfoxide or sulfone shown in Fig. 10.

In the present case the first step is expected to be the transfer of electrophilic oxygen from the monoperoxo Ti(IV) complex I of the catalyst to organic sulfide V, to yield the corresponding sulfoxide VI (reaction a) with concomitant formation of a oxotitanium intermediate II. Formation of such an oxotitanium intermediate subsequent to electrophilic oxygen transfer from a pTi complex to sulfides. has been documented in the literature [35,72,138,166–171]. The intermediate II subsequently combines with oxygen of H_2O_2 to regenerate the starting catalyst (reaction b) thus completing a catalytic cycle. The sulfoxide produced may undergo further oxidation to yield sulfone VII (reaction c) in a separate catalytic cycle of reaction.

4. Conclusions

In summary, this work highlights the synthesis and characterization of a pair of new well defined water-soluble peroxotitanium(IV) compounds anchored to linear macromolecular supports, and their successful application as highly efficient watercompatible catalysts to obtain selective conversion of sulfides to their respective sulfoxide or sulfone with H_2O_2 in aqueous medium.



Fig. 10. Proposed catalytic cycle.

The oxidation protocol being operationally simple and free from halogenated solvents or any other hazardous additive, offers the additional benefits of safety and ease of handling. Catalysts are remarkably robust in the reaction medium as evident from their easy recyclability up to 10 reaction cycles of sulfoxidation without significant change in activity. Thus, these immobilized catalysts comprising of Ti, a cheap non-toxic metal and environmentally safe water-soluble polymer supports, appear to combine the advantages of selectivity and efficiency of homogeneous catalysts with the stability and recyclability benefits of heterogeneous catalysts, making them potentially attractive for practical applications.

Acknowledgements

14

Financial support from Science and Engineering Research Board, Department of Science and Technology, New Delhi, India under Grant No. EMR/2016/003158, is gratefully acknowledged. K.A. acknowledges University Grants Commission, New Delhi, for providing her a Moulana Azad National Fellowship. We thank Dr. P. Nath and N. Chamuah, Department of Physics, Tezpur University, for their experimental help in performing the Raman spectroscopic analysis.

Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.tet.2019.130605.

References

- [1] M. Kakihana, M. Kobayashi, K. Tomita, V. Petrykin, Bull. Chem. Soc. Jpn. 83 2010) 1285.
- [2] K.A. Jørgensen, Chem. Rev. 89 (1989) 431.
- Q.H. Xia, H.Q. Ge, C.P. Ye, Z.M. Liu, K.X. Su, Chem. Rev. 105 (2005) 1603.
- X. Huali, F. Yongxian, Z. Chunhui, D. Zexue, M. Enze, G. Zhonghua, [4]
- L. Xiaonian, Chem. Biochem. Eng. Q. 22 (2008) 25. [5] N.S. Antonova, J.J. Carbó, U. Kortz, O.A. Kholdeeva, J.M. Poblet, J. Am. Chem. Soc. 132 (2010) 7488.
- [6] S. Kondo, K. Saruhashi, K. Seki, K. Matsubara, K. Miyaji, T. Kubo, K. Matsumoto, T. Katsuki, Angew. Chem. Int. Ed. 47 (2008) 10195.
- [7] T. Katsuki, K.B. Sharpless, J. Am. Chem. Soc. 102 (1980) 5974.
- [8] T. Punniyamurthy, S. Velusamy, J. Iqbal, Chem. Rev. 105 (2005) 2329.
- [9] C. Perego, A. Carati, P. Ingallina, M.A. Mantegazza, G. Bellussi, Appl. Catal., A 221 (2001) 63.
- [10] Y. Zuo, X. Wang, X. Guo, Ind. Eng. Chem. Res. 50 (2011) 8485.
- [11] Z. Shan, Z. Lu, L. Wang, C. Zhou, L. Ren, L. Zhang, X. Meng, S. Ma, F. Xiao, ChemCatChem 2 (2010) 407.
- [12] P. Wu, T. Komatsu, T. Yashima, J. Catal. 168 (1997) 400.
- [13] M.A. Mantegazza, G. Leofanti, G. Petrini, M. Padovan, A. Zecchina, S. Bordiga, Stud. Surf. Sci. Catal. 82 (1994) 541.
- [14] L. Xu, H.G. Peng, K. Zhang, H. Wu, L. Chen, Y. Liu, P. Wu, ACS Catal. 3 (2012) 103.
- [15] K.P. Bryliakov, Mini-Reviews Org. Chem. 11 (2014) 87.
- [16] X. Jia, X. Li, X. Jia, L. Xu, Y. Li, Q. Shi, T.T.L. Au-Yeung, C.W. Yip, X. Yao, A.S. Chan, Adv. Synth. Catal. 346 (2004) 723.
- [17] J. Gao, H. Guo, S. Liu, M. Wang, Tetrahedron Lett. 48 (2007) 8453. [18] O.A. Kholdeeva, G.M. Maksimov, R.I. Maksimovskaya, L.A. Kovaleva,
- M.A. Fedotov, React. Kinet. Catal. Lett. 66 (1999) 311.
- [19] Q. Zeng, S. Gao, A.K. Chelashaw, Mini-Reviews Org. Chem. 10 (2013) 198.
- [20] M.A.M. Capozzi, G. Terraneo, G. Cavallo, C. Cardellicchio, Tetrahedron 71 (2015) 4810.
- [21] G. Gao, S. Cheng, Y. An, X. Si, X. Fu, Y. Liu, H. Zhang, P. Wu, M. He, Chem-CatChem 2 (2010) 459.
- [22] V. Hulea, F. Fajula, J. Bousquet, J. Catal. 198 (2001) 179.
- [23] J.M. Fraile, C. Gil, J.A. Mayoral, B. Muel, L. Roldán, E. Vispe, S. Calderón, F. Puente, Appl. Catal., B 180 (2016) 680.
- [24] I. Fernandez, N. Khiar, Chem. Rev. 103 (2003) 3651.
- [25] H.L. Holland, Chem. Rev. 88 (1988) 473.
- [26] M.C. Carreno, Chem. Rev. 95 (1995) 1717.
- S. Patai, H. Rappoport, in: The Chemistry of Sulphones, Sulfoxides and Cyclic [27] Sulphides, 1994.
- [28] P. Metzner, A. Thuillier, in: Sulfur Reagents in Organic Synthesis, Elsevier, 2013
- [29] S. Caron, R.W. Dugger, S.G. Ruggeri, J.A. Ragan, D.H.B. Ripin, Chem. Rev. 106 (2006) 2943.
- [30] H.B. Kagan, T. Toru, C. Bolm, Asymmetric Synthesis of Chiral Sulfoxides, Wiley-VCH, Weinheim, Germany, 2008, pp. 1–29.
- [31] M.C. Carreño, G. Hernándeztorres, M. Ribagorda, A. Urbano, Chem. Commun. 41 (2009) 6129.
- [32] B. Ferber, H.B. Kagan, Adv. Synth. Catal. 38 (2007) 493.
- [33] J.X.J. Legros, R. Dehli, C. Bolm, Adv. Synth. Catal. 347 (2005) 19.
- [34] A. Lattanzi, S. Piccirillo, A. Scettri, Adv. Synth. Catal. 349 (2007) 357. [35] M.K. Panda, M.M. Shaikh, P. Ghosh, Dalton Trans. 39 (2010) 2428 (and ref-
- erences therein).
- [36] P. Pitchen, H.B. Kagan, Tetrahedron Lett. 25 (1984) 1049.
- [37] P. Pitchen, M. Desmukh, E. Dunach, H.B. Kagan, J. Am. Chem. Soc. 106 (1984) 8188
- [38] F. Di Furia, G. Modena, R. Seraglia, Synthesis (1984) 325.
- [39] H. Srour, P. Le Maux, S. Chevance, G. Simonneaux, Coord. Chem. Rev. 257 2013) 3030.
- [40] V. Hulea, A.-L. Maciuca, F. Fajula, E. Dumitriu, Appl. Catal. A 313 (2006) 200.

- [41] B.S. Lane, K. Burgess, Chem. Rev. 103 (2003) 2457.
- [42] R. Novori, M. Aoki, K. Sato, Chem. Commun. (2003) 1977.
- [43] C.W. Jones, Applications of Hydrogen Peroxide and Derivatives, Royal Society of Chemistry, Cambridge, 1999.
- [44] N. Mizuno, K. Kamata, Coord. Chem. Rev. 255 (2011) 2358.
- [45] G. Saikia, K. Ahmed, S.R. Gogoi, M. Sharma, H. Talukdar, N.S. Islam, Polyhedron 159 (2019) 192.
- [46] R.A. Frenzel, G.P. Romanelli, L.R. Pizzio, MolCatal. 457 (2018) 8.
- [47] C. Shen, J. Qiao, L. Zhao, K. Zheng, J. Jin, P. Zhang, Catal. Commun. 92 (2017) 114.
- [48] W. Zhao, C. Yang, K. Liu, Y. Yanga, T. Chang, New J. Chem. 41 (2017) 447.
- [49] J.J. Boruah, S.P. Das, S.R. Ankireddy, S.R. Gogoi, N.S. Islam, Green Chem. 15 (2013) 2944.
- [50] K. Ahmed, G. Saikia, P. Begum, S.R. Gogoi, M. Sharma, H. Talukdar, N.S. Islam, ChemistrySelect 3 (2018) 12563.
- [51] J.J. Boruah, K. Ahmed, S. Das, S.R. Gogoi, G. Saikia, M. Sharma, N.S. Islam, Mol. Catal. A: Chem. 425 (2016) 21.
- [52] R.D. Chakravarthy, V. Ramkumar, D.K. Chand, Green Chem. 16 (2014) 2190. [53] N. Gharah, S. Chakraborty, A.K. Mukherjee, R. Bhattacharyya, Inorg. Chim. Acta 362 (2009) 1089.
- [54] D.A.F. Gonçalves, R.P.R. Alvim, H.A. Bicalho, A.M. Peres, I. Binatti, P.F.R. Batista, L.S. Teixeira, R.R. Resendecd, E. Lorençon, New J. Chem. 42 (2018) 5720.
- [55] I. Tosia, C. Vurchio, M. Abrantes, I.S. Gonçalves, M. Pillinger, F. Cavani, F.M. Cordero, A. Brandi, Catal. Commun. 103 (2018) 60.
- [56] H. Egami, T. Katsuki, J. Am. Chem. Soc. 129 (2007) 8940.
- [57] P. Le Maux, G. Simonneaux, Chem. Commun. 47 (2011) 6957.
- [58] A. Fakhri, A. Naghipour, Environ. Prog. Sustain. Energy 5 (2017) 1626.
- [59] T. Karimpour, E. Safaei, B. Karimi, Y.-I. Lee, ChemCatChem 10 (2018) 1889.
- [60] S. Rayati, F. Nejabat, C R Chim. 20 (2017) 967.
- [61] M. Aghajani, E. Safaei, B. Karimi, Synth. Met. 233 (2017) 63.
- [62] H. Veisi, S. Sajjadifar, P.M. Biabri, S. Hemmati, Polyhedron 153 (2018) 240.
- [63] M.M. Najafpour, M. Amini, M. Holynska, M. Zare, E. Amini, New J. Chem. 38 (2014) 5069.
- [64] ShangS. DaiW, LiG. LvY, C. Li, S. Gao, ACS Catal. 7 (2017) 4890.
- [65] H. Srour, J. Jalkh, P. Le Maux, S. Chevance, M. Kobeissi, G. Simonneaux, J. MolCatal A Chem. 370 (2013) 75.
- [66] T. Tanaka, B. Saito, T. Katsuki, Tetrahedron Lett. 43 (2002) 3259.
- [67] B. Saito, T. Katsuki, Tetrahedron Lett. 42 (2001) 3873.
- [68] K.P. Bryliakov, E.P. Talsi, J. Mol. Catal. A: Chem. 264 (2007) 280.
- [69] I. Reviejo, V. Tabernero, M.E. Mosquera, J. Ramos, T. Cuenca, G. Jiménez, Organometallics 37 (2018) 3437 (and references therein)
- [70] M. Bonchio, G. Licini, G. Modena, O. Bortolini, S. Moro, W.A. Nugent, J. Am. Chem. Soc. 121 (1999) 6258.
- [71] M. Mba, L.J. Prins, C. Zonta, M. Cametti, A. Valkonen, K. Rissanen, G. Licini, Dalton Trans. 39 (2010) 7384.
- [72] L. Postigo, M. Ventura, T. Cuenca, G. Jiménez, B. Royo, CatalSciTechnol 5 (2015) 320.
- [73] P.K. Bera, D. Ghosh, S.H.R. Abdi, N.U.H. Khan, R.I. Kureshy, H.C. Bajaj, J. Mol. Catal. A: Chem. 361 (2012) 36.
- [74] M. Matsugi, N. Fukuda, Y. Muguruma, T. Yamaguchi, J.I. Minamikawa, S. Otsuka, Tetrahedron 57 (2001) 2739.
- [75] R.H. Wu, J. Wu, M.X. Yu, L.G. Zhu, RSC Adv. 7 (2017) 44259.
- [76] G. Boche, K. Möbus, K. Harms, M. Marsch, J. Am. Chem. Soc. 118 (1996) 2770.
- [77] X. Wang, X. Wang, H. Guo, Z. Wang, K. Ding, Chem. Eur J. 11 (2005) 4078.
- [78] J. Přech, R.E. Morris, J. Čejka, CatalSciTechnol 6 (2016) 2775.
 [79] R.H. Wu, M. Guo, M.X. Yu, L.G. Zhu, Dalton Trans. 46 (2017) 14348.
- [80] C. Bolm, O.A. Dabard, Synlett 3 (1999) 360.
- [81] M. Mba, L.J. Prins, G. Licini, Org. Lett. 9 (2007) 21.
- [82] O.A. Kholdeeva, R.I. Maksimovskaya, G.M. Maksimov, K.I. Zamaraev, React. Kinet. Catal. Lett. 63 (1998) 95.
- [83] W.T. Jin, F. Yang, L. Deng, M.L. Chen, J.F. Chen, H.B. Chen, Z.H. Zhou, Inorg. Chem. 57 (2018) 14116.
- [84] Y. Zhang, R. Tan, M. Gao, P. Hao, D. Yin, Green Chem. 19 (2017) 1182.
- [85] G. Zhao, R. Tan, Y. Zhang, X. Luo, C. Xing, D. Yin, RSC Adv. 6 (2016) 24704.
- [86] U.M. Lindström, Chem. Rev. 102 (2002) 2751.
- [87] S. Narayan, J. Muldoon, M.G. Finn, V.V. Fokin, H.C. Kolb, K.B. Sharpless, Angew. Chem. Int. Ed. 44 (2005) 3275.
- [88] C.J. Li, L. Chen, Chem. Soc. Rev. 35 (2006) 68.
- [89] M.O. Simon, C.-J. Li, Chem. Soc. Rev. 41 (2012) 1415.
- [90] U. Lindstrom, in: Marcus (Ed.), Organic Reactions in Water: Principles, Strategies and Applications, John Wiley & Sons, 2008.
- [91] P. Dixneuf, V. Cadierno, in: Metal-catalyzed Reactions in Water, John Wiley & Sons, 2013.
- [92] C.J. Li, T.H. Chan, in: Comprehensive Organic Reactions in Aqueous Media, John Wiley & Sons, 2007.
- [93] R.A. Sheldon, Catal. Today 247 (2015) 4.

Chem. 42 (2018) 5142.

React. Funct. Polym. 68 (2008) 876.

- [94] G. Cravotto, E. Borretto, M. Oliverio, A. Procopio, A. Penoni, Catal. Commun. 63 (2015) 2.
- [95] T. Kitanosono, K. Masuda, P. Xu, S. Kobayashi, Chem. Rev. 118 (2018) 679. [96] M. Sharma, G. Saikia, K. Ahmed, S.R. Gogoi, V.G. Puranik, N.S. Islam, New J.

[97] D. Kalita, S. Sarmah, S.P. Das, D. Baishya, A. Patowary, S. Baruah, N.S. Islam,

[98] S. Sarmah, D. Kalita, P. Hazarika, R. Borah, N.S. Islam, Polyhedron 23 (2004)

1097.

- [99] S.R. Gogoi, J.J. Boruah, G. Sengupta, G. Saikia, K. Ahmed, K.K. Bania, N.S. Islam, Catal. Sci. Technol. 5 (2015) 595.
- [100] J.J. Boruah, D. Kalita, S.P. Das, S. Paul, N.S. Islam, Inorg. Chem. 50 (2011) 8046. [101] J.J. Boruah, S.P. Das, R. Borah, S.R. Gogoi, N.S. Islam, Polyhedron 52 (2013)
- 246. [102] S.P. Das, J.J. Boruah, N. Sharma, N.S. Islam, J. Mol. Catal. A Chem. 356 (2012)
- 36. [103] S.P. Das, I.I. Boruah, H. Chetry, N.S. Islam, Tetrahedron Lett, 53 (2012) 1163.
- [104] P. Hazarika, D. Kalita, S. Sarmah, R. Borah, N.S. Islam, Polyhedron 25 (2006) 3501.
- [105] R.B. Merrifield, Angew Chem. Int. Ed. Engl. 24 (1985) 799.
- [106] I. Letsinger, T.E. Wagner, J. Am. Chem. Soc. 88 (1966) 2062.
- [107] D.E. Bergbreiter, Chem. Rev. 102 (2002) 3345.
- [108] A.D. Pomogailo, in: Catalysis by Polymer Immobilised Metal Complexes, Gordon and Breach Science Publishers. Amsterdam, 1998.
- [109] D. Wohrle, in: H.R. Kricheldorf (Ed.), Handbook of Polymer Synthesis, MarcelDekker, New York, 2005.
- [110] M.K. Chaudhuri, S.K. Ghosh, N.S. Islam, Inorg. Chem. 24 (1985) 2706.
- [111] B. Delley, J. Chem. Phys. 92 (1990) 508.
- [112] B. Hammer, L.B. Hansen, J.K. Norskov, Phys. Rev. 59 (1999) 7413.
- [113] W. Kohn, L.J. Sham, Phys. Rev. 140 (1965) 1133.
- [114] B. Delley, J. Chem. Phys. 92 (1990) 508.
- [115] B. Delley, J. Chem. Phys. 113 (2000) 7756.
- [116] N.A. Benedek, I.K. Snook, K. Latham, I. Yarovsky, J. Chem. Phys. 122 (2005) 144102
- [117] Y. Inada, H. Orita, J. Comput. Chem. 29 (2008) 225.
- [118] O.A. Kholdeeva, G.M. Maksimov, R.I. Maksimovskaya, L.A. Kovaleva, M.A. Fedotov, V.A. Grigoriev, C.L. Hill, Inorg. Chem. 39 (2000) 3828.
- [119] G.A. Khitrov, G.F. Strouse, J.J. Gaumet, J. Am. Soc. Mass Spectrom. 15 (2004) 260
- [120] G.C. Wang, H.H. Sung, I.D. Williams, W.H. Leung, Inorg. Chem. 51 (2012) 3640.
- [121] Y.N. Belokon, B. Green, N.S. Ikonnikov, V.S. Larichev, B.V. Lokshin, M.A. Moskalenko, M. North, C. Orizu, A.S. Peregudov, G. Timofeeva, Eur. J. Org. Chem. 14 (2000) 2655.
- [122] M. Kakihana, M. Tada, M. Shiro, V. Petrykin, M. Osada, Y. Nakamura, Inorg. Chem. 40 (2001) 891.
- [123] A. Mazzucchelli, Gazz. Chim. Ital. 37 (1907) 545.
- [124] G. Schwarzenbach, J. Muehlebach, K. Mueller, Inorg. Chem. 9 (1970) 2381.
- [125] M. Dakanali, E.T. Kefalas, C.P. Raptopoulou, A. Terzis, G. Voyiatzis, I. Kyrikou,
- T. Mavromoustakos, A. Salifoglou, Inorg. Chem. 42 (2003) 4632. [126] A. Hardy, J. D'Haen, M.K.V. Bael, J. Mullens, J. Sol. Gel Sci. Technol. 44 (2007) 65.
- [127] H. Ichinose, M. Terasaki, H. Katsuki, J. Sol. Gel Sci. Technol. 22 (2001) 33.
- [128] V. Parvanova, J. Therm. Anal. Calorim. 86 (2006) 761.
- [129] M. Tada, K. Tomita, V. Petrykin, M. Kakihana, Solid State Ion. 151 (2002) 293.
- [130] O.A. Kholdeeva, T.A. Trubitsina, R.I. Maksimovskaya, A.V. Golovin, W.A. Neiwert, B.A. Kolesov, X. López, J.M. Poblet, Inorg. Chem. 43 (2004) 2284.
- [131] V. Parvanova, J. Therm. Anal. Calorim. 130 (2017) 695.
- [132] H. Mimoun, M. Postel, F. Casabianca, J. Fischer, A. Mitschler, Inorg. Chem. 21
- (1982) 1303. [133] I. Truijen, A. Hardy, M.K.V. Bael, H.V. den Rul, J. Mullens, Thermochim. Acta 456 (2007) 38.
- [134] Q.X. Liu, Z.H. Zhou, Polyhedron 35 (2012) 1.

- [135] D.C.L. Vasconcelos, V.C. Costa, E.H.M. Nunes, A.C.S. Sabioni, M. Gasparon, W.L. Vasconcelos, in: Infrared Spectroscopy of Titania Sol-Gel Coatings on 316L Stainless Steel, 2011.
- [136] P. Zhang, Z. Zhang, W. Li, M. Zhu, Appl. Surf. Sci. 268 (2013) 381.
- [137] V.A. Zeitler, C.A. Brown, J. Phys. Chem. 61 (1957) 1174.
- [138] O.A. Kholdeeva, R.I. Maksimovskaya, J. Mol. Catal. A Chem. 262 (2007) 7. [139] K. Nakamoto, in: Infrared and Raman Spectra of Inorganic and Coordination
- Compounds, Part B, Wiley and Sons, New York, 1997. [140] G. Saikia, S.R. Gogoi, I.I. Boruah, B.M. Ram, P. Begum, K. Ahmed, M. Sharma,
- G. Ramakrishna, T. Ramasarma, N.S. Islam, ChemistrySelect 2 (2017) 5838. [141] Y.J. Liu, M. Aizawa, Z.M. Wang, H. Hatori, N. Uekawa, H. Kanoh, J. Colloid
- Interface Sci. 322 (2008) 497.
- [142] A. Bodor, I. Banyai, I. Toth, Coord. Chem. Rev. 228 (2002) 175.
- [143] Z.H. Zhou, Y.F. Deng, Z.X. Cao, R.H. Zhang, Y.L. Chow, Inorg. Chem. 44 (2005) 6912. [144] L.L.G. Justino, M.L. Ramos, M.M. Caldeira, V.M.S. Gil, Inorg. Chim. Acta 311
- (2000) 119
- [145] M. Matzapetakis, C.P. Raptopoulou, A. Terzis, A. Lakatos, T. Kiss, A. Salifoglou, Inorg Chem 38 (1999) 618
- [146] D. Bayot, B. Tinant, M. Devillers, Inorg. Chim. Acta 357 (2004) 809.
- [147] L.L.G. Justino, M.L. Ramos, M.M. Caldeira, V.M.S. Gil, Inorg. Chim. Acta 356 (2003)179
- [148] A.C. Dengel, W.P. Griffith, R.D. Powell, A.C. Skapski, J. Chem. Soc. Dalton Trans. 5 (1987) 991
- [149] S.E. Jacobson, R. Tang, F. Mares, Inorg. Chem. 17 (1978) 3055.
- [150] L. Pettersson, I. Andersson, A. Gorzsas, Coord. Chem. Rev. 237 (2003) 77.
- [151] V. Conte, F.D. Furia, S.J. Moro, Mol. Catal. 94 (1994) 323.
- [152] R.S. Sonawane, S.G. Hegde, M.K. Dongare, Mater. Chem. Phys. 77 (2003) 744. [153] C.K. Lee, D.K. Kim, J.H. Lee, J.H. Sung, I. Kim, K.H. Lee, J.W. Park, Y.K. Lee, J. Sol.
- Gel Sci. Technol. 31 (2004) 67. [154] M. Nyman, D.T. Hobbs, Chem. Mater. 18 (2006) 6425.
- [155] L. Qian, Z.L. Du, S.Y. Yang, Z.S. Jin, J. Mol. Struct. 749 (2005) 103.
- [156] V.S. Sergienko, Crystallogr. Rep. 49 (2004) 907.
 [157] D. Schwarzenbach, Inorg. Chem. 9 (1970) 239.
- [158] D. Schwarzenbach, K. Girgis, Helv. Chim. Acta 58 (1975) 2391.
- [159] W. Massa, G. Pausewang, Mater. Res. Bull. 13 (1978) 361.
- [160] F. Rajabi, S. Naserian, A. Primo, R. Luque, Adv. Synth. Catal. 353 (2011) 2060. [161] B.M. Choudary, B. Bharathi, C.V. Reddy, M.L. Kantam, J. Chem. Soc. Perkin. Trans. 1 (2002) 2069.
- [162] K. Surendra, N.S. Krishnaveni, V.P. Kumar, R. Sridhar, K.R. Rao, Tetrahedron Lett. 46 (2005) 4581.
- [163] H.G. Hosseini, S. Rostamnia, New J. Chem. 42 (2018) 619.
- [164] P.K. Bera, D. Ghosh, S.H.R. Abdi, N.U.H. Khan, R.I. Kureshy, H.C. Bajaj, J. Mol. Catal. A Chem. 361 (2012) 36.
- [165] Y. Kon, T. Yokoi, M. Yoshioka, Y. Uesaka, H. Kujira, K. Sato, T. Tatsumi, Tetrahedron Lett. 54 (2013) 4918.
- [166] Q.L. Zang, H.Y. Tang, S. Zhang, J.C. Liu, Chin. J. Chem. 26 (2008) 1435.
- Y. Goto, T. Matsui, S. Ozaki, Y. Watanabe, S. Fukuzumi, J. Am. Chem. Soc. 121 [167] (1999) 9497.
- [168] H.B. Ten Brink, A. Tuynman, H.L. Dekker, W. Hemrika, Y. Izumi, T. Oshiro, H.E. Schoemaker, R. Wever, Inorg. Chem. 37 (1998) 6780.
- [169] M. Bonchio, S. Calloni, F.D. Furia, G. Licini, G. Modena, S. Moro, W.A. Nugent, J. Am. Chem. Soc. 119 (1997) 6935.
- [170] O. Bortolini, C. Campello, F.D. Furia, G. Modena, J. Mol. Catal. 14 (1982) 63.
- [171] W. Adam, M.N. Korb, K.J. Roschmann, C. Soha-Moller, J. Org. Chem. 63 (1998) 3423.