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# 1 Introduction

The development of heterogeneous, selective oxidation catalysts that support green and energy-efficient oxidative transformations is of enormous contemporary importance, mainly owing to the mounting environmental concerns in recent times. Epoxidation of olefins is one of the pivotal reactions in organic synthesis as epoxides are valued precursors in the synthesis of a wide range of fine chemicals including pharmaceuticals, food additives, paints and epoxy resins.<sup>1</sup> Selective oxidation of sulfides to sulfoxides or sulfone represents another fundamentally and industrially

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# Polymer immobilized tantalum(v)-amino acid complexes as selective and recyclable heterogeneous catalysts for oxidation of olefins and sulfides with aqueous H<sub>2</sub>O<sub>2</sub>†

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Polymer supported heterogeneous peroxotantalum(v) catalysts were prepared by anchoring Ta(v)-diperoxo species to chloromethylated poly(styrene-divinylbenzene) resin functionalized with amino acids asparagine (L-Asn) and arginine (L-Arg). The structurally well-defined catalysts,  $[Ta(O_2)_2(L)_2]^-$ -**MR**, [L = asparagine (catalyst 1) or arginine (catalyst 2) and MR = Merrifield resin], were comprehensively characterized by elemental analysis (CHN, ICP-OES, energy dispersive X-ray spectroscopy), spectral studies (FT-IR, Raman, <sup>13</sup>C NMR, diffuse reflectance UV-vis and XPS), SEM, XRD, Brunauer–Emmett–Teller (BET) and thermogravimetric analysis (TGA). The supported peroxotantalum (pTa) compounds displayed excellent catalytic performance in epoxidation of alkenes with 30% H<sub>2</sub>O<sub>2</sub>, under solvent free reaction conditions. Styrene was epoxidized with >99% selectivity with the highest TOF of 1040 h<sup>-1</sup> obtained within 30 min reaction time, whereas the TOF for norbornene epoxidation was 2000  $h^{-1}$  within 1 h with >95% epoxide selectivity. Furthermore, the immobilized catalysts facilitated chemoselective oxidation of a broad range of organic sulfides to the desired sulfoxides with  $H_2O_2$  in methanol, under mild reaction conditions. The oxidations proceeded with a high H<sub>2</sub>O<sub>2</sub> efficiency percentage and are amenable to ready scalability. The heterogeneous catalysts could be easily recovered and reused for several consecutive catalytic cycles with undiminished activity/selectivity profiles in all cases. The developed catalytic strategies are operationally simple and, being free from halogenated solvent or any other toxic auxiliaries, environmentally clean.

important organic transformation which holds immense interest from both chemical and biological perspectives.<sup>2</sup>

A large number of promising alkene epoxidation strategies based on supported metal oxide catalysts have been developed over the years,<sup>3</sup> many of which often relied upon expensive, non-aqueous organic oxidants such as tert-butyl hydroperoxide (TBHP) and cumene hydroperoxide (CHP) along with chlorinated solvents to achieve high activity, <sup>3a,e-h,4</sup> as the presence of water often leads to poisoning of such catalysts.<sup>3e,f,4a,5</sup> Ta-Based oxidation catalysts, on the other hand, were reported to exhibit superior performance with hydrogen peroxide in comparison to organic peroxides.<sup>4a,6</sup> Silica supported Ta catalysts in particular have been documented to be inherently more selective than the analogous titanium catalysts for epoxidations with aqueous H<sub>2</sub>O<sub>2</sub>.<sup>4a,7</sup> These findings are significant in view of the current ecological concerns, which triggered an uninterrupted exploration of alternative non-polluting oxidation protocols that utilize aqueous H<sub>2</sub>O<sub>2</sub> as an oxidant,<sup>3b,4a,8</sup> an ideal waste preventing and cost effective terminal oxidant.

Catalysis by Ta compounds is a field of growing importance, as evident from the literature showing the utility of such



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#### Paper

systems in a number of organic transformations including arene hydrogenation,<sup>9</sup> polymerization,<sup>10</sup> metathesis of alkanes,<sup>11</sup> imines and olefins,<sup>12</sup> and activation of C-N bonds.<sup>13</sup> Significantly, Ta compounds have been considered ideal for 'green chemistry' applications as such systems were reported to be inert to body fluid.<sup>14</sup> Although the catalytic potential of Ta-based systems in organic oxidations is yet to be fully explored, there have been several reports pertaining to efficient Ta-based heterogeneous epoxidation catalysts supported on porous siliceous oxide or other metal oxide supports such as MCM-41 and SBA-15.3b,4a,6c-f,7,15 Such supports are, however, known to be associated with limitations with respect to catalytic activity and selectivity<sup>16</sup> and often require the incorporation of hydrophobic organic groups onto the supports.7b,16a,17 The Sharpless type silica supported chiral tantalum alkoxides coordinated with tartrate diolate systems developed by Meunier et al. are notable examples, which were shown to catalyze asymmetric epoxidation of allyl alcohol with TBHP.<sup>6d</sup> A calixarene-Ta(v) complex supported on SiO<sub>2</sub> has been reported to catalyze cyclohexene and cyclooctene epoxidation with aqueous H2O2.4a Most of the tantalum based heterogeneous oxidation catalysts could not however retain their activity and selectivity in subsequent reaction cycles.<sup>6e,15b,16a</sup> Moreover, some of these methodologies suffer from drawbacks such as low to moderate TON and selectivity, requirement of long reaction times and use of volatile organic solvents, due to which the important criterion of ecological sustainability remains a challenging issue to address. Thus, realization of high conversion under mild conditions along with catalyst recyclability is an important objective in designing supported Ta-based catalysts.

In the recent past, we have reported the synthesis and catalytic and biochemical activities of a series of peroxo complexes of d<sup>0</sup> transition metals immobilized on various polymeric supports ranging from water-soluble polymers and biopolymers to insoluble cross-linked polymer resins.<sup>18</sup> Several of these systems demonstrated excellent stability, selectivity and efficiency in a variety of organic oxidations under environmentally benign conditions.<sup>18b-d,g,h,j,k</sup> In this context, it is somewhat surprising that, notwithstanding the welldocumented advantages associated with immobilization of catalytically active transition metal species on polymer matrices such as enhancement of catalyst stability, ease of work up of the reaction mixture, and the facile regeneration and reusability of such systems,<sup>3a,19</sup> there appears to be no report available on the preparation or activity of Ta-based oxidation catalysts supported on organic polymers. Moreover, despite the availability of scores of well-defined pTa complexes in diverse ligand environments,<sup>20</sup> there still is a paucity of information regarding the activity of discrete pTa complexes as oxidation catalysts, although Ta mediated organic oxidations with H<sub>2</sub>O<sub>2</sub> have been shown to proceed via in situ formation of peroxo intermediate  $Ta(\eta^2 - O_2)$ .

In continuation of our quest for cleaner catalytic processes to accomplish organic oxidations, in the present work, we directed our efforts towards generating new heterogeneous catalysts by anchoring pTa species onto a cross-linked poly(styrene– divenylbenzene) support functionalized with amino acids asparagine and arginine. With the ability to undergo facile functionalization, in addition to its attractive attributes, viz., low cost, ready availability, and mechanical and chemical robustness, cross-linked poly(styrene-divenylbenzene) or Merrifield resin still remains one of the most popular and versatile solid supports for catalytic applications.<sup>18b,19a,22</sup> An appropriate choice of the ligand groups for functionalization of the resin is an important prerequisite for the formation of stable metalpolymer linkages which would withstand repeated catalytic cycles. Carboxylate containing ligands have been shown to be excellent co-ligands for stabilizing peroxotantalum species.<sup>20</sup> Moreover, being relatively bulky with polar side chains, the chosen amino acid ligands offered the prospect of facilitating the formation of site isolated pTa grafted stable catalysts. Metal co-ordination through the side-chain amide group of asparagine<sup>23</sup> or the guanidine moiety of arginine, which exists normally in the protonated form in solution, has rarely been observed.<sup>24</sup> The bulky multidentate ligands were demonstrated to be ideal for creating stable surface species that ensure metal atom isolation during catalytic turnover in the case of supported oxide based catalysts.4a

We describe herein the preparation and characterization of heretofore unreported polymer supported pTa catalysts and their performance in epoxidation of olefins and selective oxidation of sulfides with 30% aqueous  $H_2O_2$  with respect to their selectivity, reusability, turn over number (TON) and environmental compatibility.

# 2 Results and discussion

### 2.1 Synthesis

As illustrated in Scheme 1, preparation of immobilized peroxotantalum catalysts 1 and 2 involved a two-step synthetic protocol. Functionalization of the resin with L-Asn or L-Arg was accomplished by reacting the polymer with the respective amino acid in methanol using pyridine as a base.<sup>18b,25</sup> The solid catalysts were obtained in the subsequent step, by treating the functionalized resin with the precursor complex  $Na_3[Ta(O_2)_4]$  in the presence of 30% H<sub>2</sub>O<sub>2</sub>. Maintenance of reaction parameters such as near neutral pH, a contact time of 24 h and a reaction temperature of ca. 4 °C was found to be crucial for the desired synthesis. Chloromethylated polystyrene cross-linked with 2% divinylbenzene was chosen as the polymer support due to its superior flexibility, which usually facilitates the anchoring of metal atoms via the polymer grafted ligands.18b,22c It is important to note that the catalysts are non-hygroscopic and remain stable and active for a prolonged period.

### 2.2 Characterization

Several characterization techniques including analytical and spectroscopic methods *viz.* CHN, ICP-OES, energy dispersive X-ray spectroscopy, FT-IR, Raman, DRUV-visible spectroscopy, <sup>13</sup>C NMR, powder XRD, XPS, BET and thermogravimetric analysis were carried out to determine the structure of the catalysts.



Scheme 1 Synthesis of the chloromethylated poly(styrene-divinylbenzene) supported pTa complexes. (A) Possible structure of the polymer anchored compounds. "-----" represents the polymer chain.

As seen from the analytical data presented in Table S1 (ESI<sup>†</sup>) nearly 100% of the Cl of the  $-CH_2Cl$  groups of **MR** has been substituted by asparagine to form **MRAsn**, whereas in the case of **MRArg** *ca.* 86% of Cl was replaced by arginine. The elemental analysis data confirmed the presence of two peroxo groups per metal centre in each of the catalysts [Table S1 (ESI<sup>†</sup>)]. On the basis of the metal content obtained from EDX and ICP-OES analysis, the tantalum loading on the resin was found to be 0.37 and 0.32 mmol per gram of the polymer, for catalysts **1** and **2**, respectively. The magnetic susceptibility measurement revealed the diamagnetic nature of the catalysts in accord with the occurrence of tantalum centres in their +5 oxidation state, which was further confirmed from XPS analysis data.

**2.2.1 SEM and energy dispersive X-ray (EDX) analysis.** Scanning electron micrographs were employed in order to examine the morphological changes occurring on the surface of the polymer resin after incorporation of amino acids and subsequent anchoring of the pTa species. The micrographs revealed that the smooth surface of **MR** turned considerably coarse upon grafting of the amino acids. The attachment of the peroxo-Ta moieties on the resin resulted in further roughening of the surface with the appearance of randomly oriented deposits on the external surface of the catalysts as has been clearly observed in the micrographs (Fig. 1).

The energy dispersive X-ray analysis of the compounds carried out by focusing on multiple regions of the catalyst surface (Fig. 2) showed C, N, O, Na, and Ta as constituents of the catalysts. The results depicted in Table S1 (ESI†) are the average data obtained from these regions. The composition of the compounds derived from energy dispersive X-ray spectroscopy, which gave *in situ* analysis of the bulk, concurred well with the elemental analysis data.

**2.2.2 Powder X-ray diffraction studies.** The X-ray diffractograms of neat **MR** and pTa incorporated catalysts **1** and **2** are presented in Fig. 3. The broad peak centered at a  $2\theta$  value of *ca.*  $20^{\circ}$  observed in the diffractogram of each of these species of the complexes is characteristic of the PS-DVB resin.<sup>26</sup> The diffraction patterns of the polymeric catalysts displayed additional peaks at  $2\theta$  values of 17.9, 19.6, 20.9, 29.2, and  $30.1^{\circ}$ , which are close to the peaks observed for the peroxotantalum species (PDF 25-0861) attributable to planes (002), (012), (301), (240) and (232), respectively. That the peroxotantalum complexes are anchored onto the polymer matrix to afford the immobilized



Fig. 1 Scanning electron micrographs of (a) MR, (b) MRAsn, (c) catalyst 1, (d) MRArg and (e) catalyst 2.

catalysts **1** and **2** has thus been confirmed. Considering the intensity of the peaks for peroxotantalum species, it is also likely that there are crystallites of pTa salt present in the resin in addition to the covalently anchored pTa compounds. This is also in accord with the roughening seen in the scanning electron micrograph of the compounds.

**2.2.3** X-ray photoelectron spectroscopy. The XPS spectra of the pTa incorporated complexes 1 and 2 are presented in Fig. 4. XPS is an effective tool for studying the electronic properties of the species formed on the surface. The complexes displayed typical  $4f_{5/2}$  and  $4f_{7/2}$  peaks at binding energies of 27.8 and 26.2 eV.



Fig. 2 EDX spectra of complexes (a) 1 and (b) 2



Fig. 3 X-ray diffraction (XRD) pattern of (a) **MR**, (b) catalyst **1**, (c) catalyst **1** after the 5th cycle, (d) catalyst **2** and (e) catalyst **2** after the 5th cycle.

The values are in good agreement with the available literature data for tantalum in the +5 oxidation state.<sup>27</sup> The O1s peak at 532.0 eV was attributed to the oxygen from metal peroxide.<sup>28</sup> Thus, XPS analysis confirms the presence of peroxotantalum(v) species on the surface of the polymeric catalysts. The XPS results are in accord with the diamagnetic nature of the complexes, as indicated by the magnetic susceptibility measurements.

**2.2.4 BET analysis.** The surface areas of the functionalized resin and metal incorporated polymers were determined by using BET analysis with the nitrogen adsorption method.<sup>29</sup> The BJH model was used to determine the pore volume.<sup>30</sup> The N<sub>2</sub> adsorption/desorption isotherms of the samples displayed typical type II adsorption of an IUPAC standard on particles with macropores or nonpores showing poor adsorption.<sup>31</sup> The result presented in Table 1 shows that after amino acid incorporation on the resin, the surface area of **MR** was decreased from 11.5 to 9.6 and 10.8 m<sup>2</sup> g<sup>-1</sup> for the functionalized resins **MRAsn** and **MRArg**, respectively. A further decrease in the catalyst surface area was observed after incorporation of pTa moieties, which is likely to be due to the pore blockage resulting from the functionalization followed by attachment of peroxometal species to the resin.<sup>18b,32</sup>



Fig. 4 XPS spectra of Ta (4f\_{5/2}) and (4f\_{7/2}) peaks for (a) catalyst  ${\bf 1}$  and (b) catalyst  ${\bf 2}.$ 

Table 1 BET surface area,  $V_{tot}$  and pore radius of MR, amino acid linked MR and polymer-bound catalysts 1 and 2

Compound	$S_{\mathrm{BET}}^{a} \left(\mathrm{m}^{2} \mathrm{g}^{-1}\right)$	$V_{\rm tot}^{\ \ b} \left( {\rm cc} \ {\rm g}^{-1} \right)$	Pore radius (Å)
MR	11.5	0.12	53.7
MRAsn	9.6	0.10	39.9
Catalyst 1	5.5	0.068	40.1
MRArg	10.8	0.013	22.7
Catalyst 2	10.7	0.10	49.0
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<sup>*a*</sup> BET surface area. <sup>*b*</sup> Total pore volume.

**2.2.5 IR and Raman spectral analysis.** A comparative evaluation of FTIR and Raman spectral analysis data of the host **MR**, the amino acid grafted resin and the immobilized catalysts demonstrated that covalent anchoring of the amino acids to the polymer and subsequent anchoring of the pTa moieties to the functionalized resin was successful. The FTIR and the complementary Raman spectra of each of these polymeric compounds are presented in Fig. 5, Fig. 6 and Fig. S2 (ESI†), and their significant features along with empirical assignments based on available relevant literature are outlined in Table S2 (ESI†).<sup>18,20a,25,33</sup>

Typical of the spectra of pristine polymer **MR**, the amino acid functionalized polymers and metal-anchored catalysts are the absorptions in the vicinity of *ca.* 3050, 2920, 1025 and 690 cm<sup>-1</sup>, due to the  $\nu_{aromatic}$ (CH),  $\nu_{aliphatic}$ (CH),  $\delta_{aromatic in-plane}$ (CH) and  $\delta_{aromatic out-of-plane}$ (CH) vibrations.<sup>18b,25,33a,c</sup> An intense band at *ca.* 1264 cm<sup>-1</sup> observed in the spectrum of **MR** has been ascribed to the  $\nu$ (C–Cl) mode of the –CH<sub>2</sub>Cl moiety.<sup>25,33a</sup> Anchoring of a ligand group on Merrifield resin by replacement of the Cl atom from the –CH<sub>2</sub>Cl group can be monitored conveniently by observing the change in intensity or disappearance of the intense  $\nu$ (C–Cl) mode of the –CH<sub>2</sub>Cl moiety.<sup>25,33a</sup> In the spectrum of the functionalized polymers **MRAsn** and **MRArg**, the near disappearance of the  $\nu$ (C–Cl) band thus indicated replacement of Cl from the –CH<sub>2</sub>Cl group of **MR** with the amino acid ligands. Further evidence regarding the grafting



Fig. 5  $\,$  IR spectra of (a) MRAsn, (b) catalyst 1 and (c) catalyst 1 after the 5th cycle of reaction.

of the amino acid to the polymer could be derived from the observance of additional bands in the spectra in the 1650 to 1580 cm<sup>-1</sup> region, although the spectral patterns appeared quite complex with a number of bands of the ligands occurring in an overlapping region.<sup>33d</sup>

The intense band observed at 1629 cm<sup>-1</sup> in the IR spectrum of **MRAsn** has been ascribed to the  $\nu$ (C=O) (amide I) band, as this absorption is the most prominent one in the asparagine spectrum.<sup>34</sup> The band due to  $\delta$ (NH<sub>3</sub><sup>+</sup>) observed at *ca.* 1680 cm<sup>-1</sup> in the spectrum of free asparagine was absent in the spectrum of polymer bound **MRAsn**, indicating the participation of the group in bond formation with the polymer.<sup>34*a*</sup> In addition, the appearance of a new band at 1085 cm<sup>-1</sup> for  $\nu$ (C–N) indicated the formation of a carbon–nitrogen bond by replacing the chloride group of the host resin.<sup>18*b*,25,33*a*</sup> The absorptions attributable to  $\nu_{asym}$ (COO) and  $\nu_{sym}$ (COO) bands of the amino acid occurred at 1598 and 1422 cm<sup>-1</sup>, respectively, in **MRAsn**.<sup>34</sup>

Upon incorporation of peroxotantalum species onto the functionalized polymers, new well-resolved bands representing the characteristic  $\nu$ (O–O) modes of the  $\eta^2$ -peroxo group, along





with metal oxygen symmetric and asymmetric stretching vibrations, appeared in both the IR and Raman spectra of catalysts 1 and 2, in the expected 850–800 cm<sup>-1 20a,d</sup> and 500–600 cm<sup>-1</sup> region, respectively.<sup>20a,35</sup> In contrast to the IR spectrum of the starting sodium tetraperoxotantalate complex, which exhibited a single absorption at around 820 cm<sup>-1</sup> attributable to the  $\nu$ (O–O) vibration, the IR as well as Raman spectra of both the catalysts displayed two distinct peaks corresponding to the  $\nu$ (O–O) mode in the 800–850 cm<sup>-1</sup> region. The observed spectral pattern is typical of diperoxotantalum species as has been reported previously.<sup>20a,35a</sup>

For the pTa complex **1**, the  $\nu$ (CO) modes of the amino acid side chain remained unaltered at 1630 cm<sup>-1</sup> ruling out the possibility of involvement of the –CONH<sub>2</sub> group in metal complexation. Participation of the carboxylate group in co-ordination was indicated by a slight shift observed in the  $\nu_{asym}$ (COO) mode to a higher frequency of 1601 cm<sup>-1</sup> along with the appearance of a medium intensity band at 1353 cm<sup>-1</sup> attributable to  $\nu_{sym}$ (COO) shifted to lower frequency due to complexation.<sup>36</sup> Thus, the increase in the difference between asymmetric and symmetric stretching of the carboxylate group ( $\Delta \nu = 248$  cm<sup>-1</sup>) compared to that of the free ligand ( $\Delta \nu = 176$  cm<sup>-1</sup>) indicated unidentate co-ordination of the carboxylate group to the Ta(v) centre of immobilized catalyst **1**.<sup>18*b*,37</sup>

The IR spectrum of **MRArg** as well as its metal incorporated analogue catalyst 2 displayed bands at *ca.* 1627, 1599, 1421, and 1089 cm<sup>-1</sup>, which were ascribed to  $\nu_{sym}(CN_3H_5^+)$ ,  $\nu_{asym}(COO)$ ,  $\nu_{sym}(COO)$ , and  $\nu_{sym}(C-N)$  vibrations on the basis of literature findings.<sup>38</sup> The band due to the  $\nu_{sym}(CN_3H_5^+)$  mode does not shift significantly after metal complexation, suggesting the non-participation of the guanidine group in co-ordination. An indication of co-ordination of the carboxylate group to the Ta(v) centre in a unidentate fashion was obtained from the observance of a band attributable to  $\nu_{\rm sym}$ (COO) at a relatively lower frequency of 1352 cm<sup>-1</sup>, although the exact shifting of the corresponding  $\nu_{\rm asym}$ (COO) mode could not be determined with certainty, due to overlapping of the region with the symmetric stretching frequency of the guanidine moiety.

Both the complexes showed bands near 1710 cm<sup>-1</sup> depicting the presence of free –COOH groups in the compound. Broad and strong  $\nu$ (OH) bands displayed at 3400–3500 cm<sup>-1</sup> showed the presence of lattice water in the complex. Due to the overlapping of  $\nu$ (N–H) vibrations with  $\nu$ (OH) modes of lattice water, these bands could not be assigned with certainty.

**2.2.6 Electronic spectral studies.** The diffuse reflectance UV-visible spectra of complexes **1** and **2** showed two distinct peaks in the region 270–380 nm [Fig. S3 and S4 (ESI<sup>†</sup>)]. The peak at 279 nm was attributed to the  $\pi \rightarrow \pi^*$  transition in the polymeric resin,<sup>39</sup> while a new peak was observed in both the complexes at around 380 nm. This characteristic absorption of peroxotantalum species was ascribed to the peroxo to metal charge transfer band (LMCT) on the basis of the available literature.<sup>28</sup>

**2.2.7** <sup>13</sup>C NMR analysis. The <sup>13</sup>C NMR spectra of catalysts 1 and 2 recorded in the solid state are presented in Fig. 7 and Fig. S5 (ESI<sup>†</sup>), respectively. The corresponding resonances along with those of free MR as well as functionalized resins MRAsn and MRArg are provided in Table S3 (ESI<sup>†</sup>) for comparison. The assignments have been made based on reported data although<sup>18b,40</sup> there may be slight variations in the exact resonance positions depending on the NMR technique used *viz.*, solid or liquid state analysis. The resin after functionalization displayed typical resonances corresponding to the respective amino acid along with peaks due to quaternary aromatic,



ig. 7 Solid state <sup>13</sup>C NMR spectra of (a) **MRAsn** and (b) catalyst **1**.

protonated aromatic and aliphatic methine carbons of pristine **MR**.<sup>40b</sup> The absence of signal at *ca.* 46 ppm due to the  $-CH_2Cl$  group and appearance of a new signal at around 64 ppm attributable to amine bound methylene carbon evidenced the replacement of Cl from  $-CH_2Cl$  with the amino acid to form C–N bonds.<sup>18b,41</sup> By analogy with the <sup>13</sup>C spectrum of free asparagine, two closely spaced peaks observed at 181 and 179 ppm in the case of **MRAsn** have been assigned to free carboxylate and amide C atoms, respectively. The spectrum of **MRArg** also displayed a resonance due to the carboxylate C atom at 181 ppm.

After anchoring of the metal complex to the functionalized resins, the intensity of the carboxylate carbon resonance at ca. 181 ppm was observed to decrease in the spectra of both the catalysts and an additional peak appeared at considerably lower field of 219 ppm. The new resonance is characteristic of a complexed carboxylate carbon, indicative of the metal incorporation through the carboxylate group. The significant downfield shift of nearly 39 ppm ( $\Delta \delta = \delta_{\text{complex}} - \delta_{\text{free carboxylate}}$ ) relative to the free carboxylate peak reflected strong metal ligand interactions, as has also been observed previously in the case of peroxo-Mo anchored valine and alanine functionalized MR.<sup>18b</sup> In fact, previous reports showed that <sup>13</sup>C NMR chemical shifts induced by co-ordination have been widely used as a tool to interpret the mode of bonding of the co-ligands in peroxometal compounds.<sup>42</sup> The nearly unaltered position of the guanidyl carbon resonance in the spectrum of catalyst 2 at ca. 167 ppm negated the possibility of participation of the guanidyl group of arginine in metal co-ordination.<sup>43</sup>

**2.2.8 Thermogravimetric analysis.** Thermograms of the pTa loaded catalysts **1** and **2** revealed a close analogy with the decomposition pattern of the respective functionalized polymers **MRAsn** and **MRArg**. The compounds undergo multistage degradation upon heating up to a temperature of 700 °C (Fig. 8). As seen in Table S4 (ESI†) in the case of **MRAsn** and **MRArg**, the degradation step occurring between room temperature and *ca.* 100 °C, due to the loss of water of crystallization, was followed by a weight loss of 12.5% and 9.4% in the temperature range of 148–257 °C and 155–239 °C, respectively. This degradation has been attributed to the release of amino acids from the polymer, based on available reports on the thermal



Fig. 8 TG plot of (a) catalyst 1 and (b) catalyst 2.

decomposition characteristics of amino acids.<sup>44</sup> The decomposition observed in the temperature range of 284–700  $^{\circ}$ C was due to the degradation of the base polymer.<sup>45</sup>

In the thermograms of catalysts 1 and 2, a degradation subsequent to the initial dehydration step, occurring in the range of 104-146 °C and 104-145 °C, respectively, has been ascribed to the loss of peroxo groups from the [Ta(O<sub>2</sub>)<sub>2</sub>] moieties anchored to the polymer. The degradation corresponding to release of amino acids from compounds 1 and 2 occurred in the temperature range of 147-299 °C and 150-291 °C, respectively. The remaining resin degraded in the temperature range of 300-700 °C with a weight loss of 59.9% and 61.6%, respectively, from complexes 1 and 2. The black residue obtained after complete degradation of the complexes was analyzed with IR spectral analysis and was devoid of any significant bands of the peroxo group, the amino acid and the polymer matrix. Thus it has been confirmed that the residue remaining after degradation of the catalysts consisted of the oxotantalum compound along with the char residue of the polymer.

### 2.3 Catalytic activities of the supported complexes 1 and 2

2.3.1 Alkene epoxidation. The catalytic performance of the pTa complexes in alkene epoxidation was examined by conducting exploratory experiments using styrene epoxidation as a probe reaction in a variety of solvents as well as without solvent. With an aim to optimize the reaction conditions for maximum alkene conversion, the influence of reaction parameters such as catalyst amount, oxidant concentration, solvent nature, temperature and time was investigated using complex 1 as a representative catalyst. The results presented in Table 2 and Fig. 9 illustrate that the epoxidation reaction conducted under solvent free conditions, maintaining a Ta: styrene molar ratio of 1:1000 with 30% H<sub>2</sub>O<sub>2</sub> as a terminal oxidant (2 equivalents), proceeded smoothly to provide good styrene conversion with  $\geq$  99% epoxide selectivity within 2 h [Fig. 9 and Table 2 (entry 5)]. To investigate the solvent effect, apart from water, we have chosen relatively safe organic solvents, omitting the use of perilous chlorinated solvents. Interestingly, the epoxide was obtained as the sole reaction product in each of the tested solvents under similar reaction conditions, despite the relatively lower conversions obtained in the presence of solvent. The likely cause of the greater efficiency of the solvent free procedure appears to be the reduced mobility experienced by the reactants in the absence of solvent in the reaction mixture. Based on these results, we have opted to study the activity of the catalysts

Table 2 Effect of solvent on styrene oxidation with 30%  ${\rm H_2O_2}$  catalyzed by complex  ${\bf 1}$ 

Entry	Solvent	Conversion (%)	Epoxide selectivity (%)	TON
1	$H_2O$	27	≥99	270
2	$CH_3OH$	8	100	80
3	$C_2H_5OH$	8	100	80
4	CH <sub>3</sub> CN	6	100	60
5	_	83	$\geq$ 99	830

<sup>*a*</sup> TON (turn over number) = mmol of product per mmol of catalyst.



Fig. 9 Effect of solvent on styrene conversion. Reaction conditions: styrene (5 mmol), catalyst 1 (0.005 mmol of Ta, 13.5 mg), 30%  $H_2O_2$  (10 mmol, 1.13 mL), 60 °C, solvent (5 mL), 2 h.

Table 3 Effect of temperature on styrene oxidation with 30%  ${\rm H_2O_2}$  catalyzed by complex 1

Entry	Temperature	Conversion (%)	Epoxide selectivity (%)	TON
1	RT	5	100	50
2	40	20	$\geq 99$	200
3	60	83	$\geq 99$	830
4	80	91	$\geq 99$	915

in epoxidation without addition of any solvent for the subsequent reactions.

Next, we have examined the influence of temperature on the reaction rate by conducting the reaction under four different temperature conditions keeping the other variables constant (Table 3 and Fig. 10). While there was only 5% conversion at room temperature [Fig. 10 and Table 3 (entry 1)], a significant leap in the rate of styrene conversion was observed at a moderately elevated temperature of 60 °C [Fig. 10 and Table 3 (entry 3)]. On increasing the temperature further to 80 °C, 91% conversion of styrene could be attained within 2 h [Fig. 10 and Table 3 (entry 4)]. Thus in order to obtain the highest TON and TOF, without affecting the epoxide selectivity, the reaction temperature of 80 °C appeared to be optimal.



Fig. 10 Effect of temperature on styrene conversion. Reaction conditions: styrene (5 mmol), catalyst 1 (0.005 mmol of Ta, 13.5 mg), 30%  $\rm H_2O_2$  (10 mmol, 1.13 mL), 2 h.

Table 4 Effect of  $H_2O_2$  concentration on styrene oxidation catalyzed by complex **1** 

Entry	$H_2O_2$ (equiv.)	Conversion (%)	Epoxide selectivity (%)	TON
1	1	84	$\geq 99$	844
2	2	91	$\geq 99$	915
3	3	90	$\geq 98$	898
4	4	88	$\geq 98$	880
5	5	79	$\geq 98$	790
6	6	65	$\geq 98$	652
7	8	50	$\geq 98$	500



Fig. 11 Effect of  $H_2O_2$  concentration on styrene conversion. Reaction conditions: styrene (5 mmol), catalyst 1 (0.005 mmol of Ta, 13.5 mg), 80 °C, 2 h.

A systematic screening of the effect of oxidant concentration was subsequently performed using seven different equivalents of 30% H<sub>2</sub>O<sub>2</sub> ranging from 1-8 with respect to the substrate under otherwise identical reaction conditions. As can be seen from Table 4 and Fig. 11, an interesting trend with respect to the % conversion of styrene versus oxidant concentration emerged, although the epoxide selectivity remained close to 99% irrespective of the amount of H<sub>2</sub>O<sub>2</sub> used. An increase in the H<sub>2</sub>O<sub>2</sub> concentration from 1 to 2 equivalents led to a rise in the conversion of styrene from 84 to 91%, providing a reasonably good TON of 915 [Fig. 11 and Table 4 (entry 2)]. However, on a further increase of the oxidant a gradual decline in the overall styrene conversion was noted. Thus, styrene:  $H_2O_2 = 1:2$ was regarded as the optimal ratio for styrene conversion. Dilution of the reacting species occurring due to the increasing volumes of H<sub>2</sub>O<sub>2</sub> added to the reaction mixture beyond the optimum requirement is likely to be responsible for the aforementioned observation. Previous reports, including our own past experiences with organic oxidations, reveal that such a dilution effect is not unusual in the case of metal catalyzed H<sub>2</sub>O<sub>2</sub> induced organic oxidations.<sup>46</sup>

The reaction was further optimized with respect to the catalyst amount and the results are shown in Table 5 and Fig. 12. The conversion increased to nearly 100% as the catalyst loading increased while maintaining high selectivity. A catalyst : substrate ratio of 1:2000 was considered as ideal for achieving high TON along with complete epoxide selectivity in the presence of 2 equivalents of  $H_2O_2$  [Fig. 12 and Table 5 (entry 4)]. The result

Table 5 Effect of catalyst amount on styrene oxidation with 30%  ${\rm H_2O_2}$  catalyzed by complex 1

Ent	ry Molar ratio (1	Га:Sty) Conversio	on (%) Epoxide select	tivity (%) TON
1	1:500	95	$\geq 98$	477
2	1:1000	91	$\geq 99$	915
3	1:1500	80	$\geq 99$	1201
4	1:2000	69	$\geq 99$	1384
5	—	$11^a$	$\geq 99$	
6	1:2000	$24^b$	$\geq 99$	480

 $^a$  Blank experiment without any catalyst.  $^b$  Using Na\_3[Ta(O\_2)\_4]·H\_2O as the catalyst (1.0 mg, 0.0025 mmol Ta).



Fig. 12 Effect of catalyst amount (catalyst 1) on styrene conversion. Reaction conditions: styrene (5 mmol), 30%  $H_2O_2$  (10 mmol, 1.13 mL), 80 °C, 2 h.

of a blank reaction conducted under catalyst free conditions provided just 11% conversion of styrene within the stipulated reaction time [Fig. 12 and Table 5 (entry 5)]. Moreover, significantly lower conversion was obtained using free unsupported pTa complex  $Na_3[Ta(O_2)_4]$  as the catalyst [Fig. 12 and Table 5 (entry 6)]. That the enhanced activity displayed by the solid catalysts 1 and 2 is a consequence of immobilization of the pTa species on a polymer support is evident from these observations.

The progress of the reaction monitored within a time span of 0.5 to 6 h showed a gradual increase in styrene conversion till the completion of the reaction occurring at 6 h [Table 6 and Fig. 13]. The observation clearly indicated that the catalyst retained its high activity and epoxide selectivity at an elevated temperature of 80  $^{\circ}$ C even on prolonging the reaction up to 6 h.

Table 6 Effect of reaction time on styrene oxidation with 30%  ${\rm H_2O_2}$  catalyzed by complex 1

Entry	Time (h)	Conversion (%)	Epoxide selectivity (%)	TON	${\mathop{\rm TOF}^a}{\left( {{{ m{h}}^{ - 1}}}  ight)}$
1	0.5	26	≥99	520	1040
2	1	27	$\geq 99$	553	553
3	2	69	$\geq 99$	1384	692
4	3	71	$\geq 99$	1386	462
5	4	87	$\geq 99$	1738	434
6	6	100	$\geq 99$	2000	333

 $^a$  TOF (turn over frequency) = mmol of product per mmol of catalyst per hour.



Fig. 13 Effect of reaction time on styrene conversion. Reaction conditions: styrene (5 mmol), catalyst amount (0.0025 mmol of Ta, 6.8 mg), 30%  $H_2O_2$  (10 mmol, 1.13 mL), 80 °C.

Significantly, at 0.0025 mmol of catalyst the initial TOF of approximately 1040  $h^{-1}$  was obtained within 30 min of starting the reaction [Fig. 13 and Table 6 (entry 1)].

Determination of the utilization efficiency of hydrogen peroxide or the effective use of  $H_2O_2$  in the oxidation process is of great interest as many transition metal catalysts are known to decompose  $H_2O_2$  at elevated temperatures.<sup>15*a*,47</sup> The  $H_2O_2$ efficiency percentage (defined as: 100 × moles of  $H_2O_2$  consumed in the formation of the oxidized product/moles of  $H_2O_2$ converted)<sup>48</sup> [Text S1 (ESI†)] for epoxidation of styrene in the present study was found to be 88%, which is reasonably high considering that the reaction was conducted at 80 °C and required 6 h for completion. It is also notable that we have ascertained the potential of the catalytic methodologies developed for alkene epoxidation for relatively larger scale synthetic applications by conducting the styrene epoxidation reaction at ten-fold scale under the optimized conditions (Table 7, entry 1<sup>f</sup>).

Subsequent to optimization of the reaction conditions for epoxidation of styrene, a conjugated olefin, we proceeded to explore the potential of the catalytic procedure for wider applications and the results are summarized in Table 7. Both the pTa catalysts were found to be highly effective in the epoxidation of cyclohexene and norbornene, which occurred at a much faster rate compared to styrene epoxidation. It is generally assumed that oxidation of terminal alkenes is difficult owing to the presence of electron deficient double bonds.<sup>49</sup> As shown in Table 7, norbornene, a relatively bulky cyclic olefin, was epoxidized with 95% selectivity under the reaction conditions optimized for styrene epoxidation. Epoxidation of norbornene has been receiving a great deal of interest owing to the utility of its epoxide as pharmaceutical intermediates and in polymer synthesis.<sup>50</sup> No report appears to exist on norbornene epoxidation mediated by Ta-based catalysts. In the case of cyclohexene, 100% conversion was achieved within 1 h, however the selectivity towards the epoxide was observed to be moderate with formation of diol as a secondary product.

2.3.2 Sulfide oxidation. The encouraging results achieved in the case of alkene epoxidation under solvent-less conditions prompted us to explore the catalytic performance of compounds 1 and 2 in sulfide oxidation in the absence of solvent. Accordingly, an initial reaction was carried out with thioanisole as the model substrate by maintaining a catalyst:substrate molar ratio of 1:1000 and substrate: oxidant molar ratio of 1:2 under solvent free conditions at room temperature. Under these conditions, the oxidation proceeded rapidly (a TOF of 601  $h^{-1}$ ) (Table S5, entry 1, ESI<sup>†</sup>), hence the reaction afforded a mixture of the sulfoxide and sulfone. We have subsequently screened the reaction in the presence of different solvents and examined the effect of various reaction parameters on the rate of the reaction in Table S5 (ESI<sup>†</sup>). MeOH emerged to be the best solvent for attaining complete oxidation of MPS with 100% sulfoxide selectivity within 40 min reaction time using 4 equivalents of H<sub>2</sub>O<sub>2</sub>. Although a high TON of 1920 could be obtained with a substantially low catalyst loading (Ta:S = 1:2000), a catalyst:substrate molar ratio of 1:1000 was found to be optimal to obtain a high TOF without compromising the sulfoxide selectivity (Table S5, entry 8, ESI†). The oxidation reaction conducted in the absence of the catalyst in a control experiment provided a very low yield (14%) with poor selectivity (Table S5, entry 12, ESI<sup>+</sup>), whereas in the presence of the neat unsupported pTa complex Na<sub>3</sub>[Ta(O<sub>2</sub>)<sub>4</sub>]·H<sub>2</sub>O, the yield was 38% (Table S5, entry 13, ESI†). It is also notable that, despite the considerable rate enhancement of the reaction

Table 7 Selective oxidation of alkenes to epoxides with 30% H<sub>2</sub>O<sub>2</sub> catalyzed by catalysts 1 and 2<sup>a</sup>

		Catalyst 1	L					Catalyst 2	2				
				Selectivit	ty					Selectivit	ty		
Entry	Substrate	Time (h)	Conversion (%)	Epoxide	Others	$TON^b$	$\operatorname{TOF}^{c}\left(h^{-1}\right)$	Time (h)	Conversion (%)	Epoxide	Others	$TON^b$	$\operatorname{TOF}^{c}\left( \mathrm{h}^{-1} ight)$
1	$\frown$	6 6	$100 \\ 99^{e}$	99 99	$1^d$ $1^d$	2000 1980	333 330	6 6	84 82 <sup>e</sup>	97 95	$3^d$ $5^d$	1680 1640	280 273
		6	$100^{f}$	99	$1^d$	2000	333	6	$84^f$	97	$3^d$	1680	280
2	$\bigcirc$	1	100	68	32 <sup>g</sup>	2000	2000	2	100	66	$34^h$	2000	1000
3	À	1	100	95	5 <sup><i>i</i></sup>	2000	2000	1.5	100	94	6 <sup><i>i</i></sup>	2000	1333

<sup>*a*</sup> Reactions were carried out with 5 mmol of substrate and 10 mmol of 30%  $H_2O_2$  without solvent at 80 °C. Catalyst (0.0025 mmol of Ta). <sup>*b*</sup> TON (turn over number) = mmol of product per mmol of catalyst. <sup>*c*</sup> TOF (turn over frequency) = mmol of product per mmol of catalyst per hour. <sup>*d*</sup> Benzaldehyde. <sup>*e*</sup> % conversion for the 5th reaction cycle. <sup>*f*</sup> Scale-up reaction (5.7 g). <sup>*g*</sup> 2-Cyclohexen-1-ol = 1.7%, 2-cyclohexen-1-one = 3.7%, cyclohexane-1,2-diol = 26.6%. <sup>*h*</sup> 2-Cyclohexen-1-ol = 1.9%, 2-cyclohexen-1-one = 3.2%, cyclohexane-1,2-diol = 28.9%. <sup>*i*</sup> Norbornanone.

Table 8 Selective oxidation of sulfides to sulfoxides with 30% H<sub>2</sub>O<sub>2</sub> catalyzed by catalysts 1 and  $2^a$  at room temperature

		R <sup>1</sup>	$S_{R^2} = \frac{Catalys}{30\% H_2O_2}$	st 1 or 2 (1 (4 equiva	ներություն ներ հերությնուն հերություն ներ հերություն հերություն հերություն հերություն հերություն հերություն հերություն հեր հերություն հերություն հերություն հերություն հերություն հերություն հերություն հերություն հերություն հերություն հ		R <sup>2</sup>		
		Catalyst 1				Catalyst 2			
Entry	Substrates	Time (min)	Isolated yield (%)	$TON^b$	$\mathrm{TOF}^{c}\left(\mathrm{h}^{-1} ight)$	Time (min)	Isolated yield (%)	$TON^b$	$\mathrm{TOF}^{c}\left(\mathrm{h}^{-1} ight)$
1	S_	40 40 40	97 96 <sup>d</sup> 96 <sup>e</sup>	970 960 960	1447 1432 1432	70 70 70	95 97 <sup>d</sup> 96 <sup>e</sup>	950 970 960	812 829 820
2	∕s∖	25	98	980	2333	40	97	970	1448
3	$\sim$ s $\sim$	40	94	940	1402	70	96	960	820
4	S_	45	96	960	1280	80	95	950	714
5	S	40	97	970	1448	70	97	970	829
6	ССССОН	195	94	940	289	220	94	940	256
7	S,	210	95	950	271	240	98	980	245
8	C <sup>s</sup> C	360	53	530	88	360	51	510	85

<sup>*a*</sup> All the reactions were carried out with 5 mmol of substrate and 20 mmol of 30% H<sub>2</sub>O<sub>2</sub> in 5 mL of solvent at RT. Catalyst (0.005 mmol of Ta). <sup>*b*</sup> TON (turn over number) = mmol of product per mmol of catalyst. <sup>*c*</sup> TOF (turn over frequency) = mmol of product per mmol of catalyst per hour. <sup>*d*</sup> % conversion for the 5th reaction cycle. <sup>*e*</sup> Scale-up data (7.5 g of MPS).

conducted at 60  $^{\circ}$ C, the selectivity of the reaction system was found to diminish with the formation of both the sulfoxide and sulfone (Table S5, entry 14, ESI†). Thus ambient temperature was found to be more favorable for the sulfoxidation reaction, in contrast to the epoxidation reaction, where the best results were obtained at a relatively elevated temperature.

A broad range of structurally diverse sulfides were subjected to the standardized catalytic methodology in the presence of each of the catalysts **1** and **2** under optimized conditions. The data presented in Table 8 demonstrate that all the tested substrates were effectively oxidized to form the respective sulfoxide as the exclusive product in excellent yield and TOF. Catalyst **1** showed relatively superior performance compared to catalyst **2**, as has been observed in the case of the epoxidation reaction. The lower activity of catalyst **2** may be attributed to the presence of relatively bulky guanidine groups of arginine side chains, due to which the Ta bound peroxo groups are probably less readily accessible to the approaching substrate, compared to catalyst **1**.

Our findings also revealed several attractive features of the developed environment friendly catalytic protocol. Importantly, no overoxidation of the sulfoxide to the sulfone occurred for any of the tested substrates under these conditions even on prolonging the reaction. It is further evident that dialkyl-sulfides (Table 8, entries 2 and 3) were more readily oxidized compared to less nucleophilic conjugated systems such as aromatic and allylic sulfides. As thioether oxidation by  $H_2O_2$  has been known to generally proceed *via* electrophilic addition of an oxygen atom to the substrate,<sup>51</sup> the observed variation in

the rates of oxidation displays the expected trend, which is also in accord with previous literature.<sup>18b-d,g,h,j,k</sup>

The catalysts displayed excellent chemoselectivity, as exemplified by oxidation of allylic and alcoholic sulfides (Table 8, entries 6 and 7) to afford the corresponding sulfoxide as the sole product without effecting other oxidation prone functional groups, such as the C=C bond or -OH group. Moreover, the  $H_2O_2$  efficiency percentage was observed to be consistently high (94–97%) in the presence of both catalysts 1 and 2 for the sulfoxidation reactions. The milder reaction conditions employed for oxidation of sulfides (*viz.*, room temperature and a relatively shorter reaction time) are likely to be responsible for the relatively higher  $H_2O_2$  efficiency observed in sulfoxidation comparison to styrene oxidation. The developed sulfoxidation procedure was also found to be amenable to ready scalability (Table 8, entry 1<sup>e</sup>), as has been found in the case of the epoxidation reaction.

2.3.3 Test for heterogeneity of the reactions. The heterogeneous nature of the catalytic processes was confirmed by conducting independent experiments using MPS or styrene as the substrate representing each type of transformation. After completion of the reaction and separating the solid catalyst, the filtrate obtained was treated with a fresh batch of reagents. The reactions were allowed to run for a further 2 h without the catalyst. That none of the catalytic reactions proceeds after removal of the catalyst from the reaction mixture was evident, as the conversions were found to be <18% in the case of styrene epoxidation, whereas for MPS oxidation it was <15%. These values are quite close to the ones obtained for the respective Conversion %

0

1



4

5



3

Run

2

blank experiments. Furthermore, the possibility of metal leaching out of the support could be ruled out as the ICP-OES analysis of the filtrate showed no sign of metal presence.

**2.3.4 Recyclability of the catalysts.** The immobilized catalysts enabled easy and efficient recovery from the spent reaction mixture by simple filtration or centrifugation. The recovered catalyst, after washing with acetone and drying under a vacuum, was recharged in the subsequent reaction run without further conditioning. The catalyst recyclability in olefin epoxidation and oxidation of thioether was probed independently using styrene or MPS under the respective optimized reaction conditions, up to five consecutive cycles of oxidation in each case.

The results given in Table 7 (entry 1<sup>e</sup>) and Table 8 (entry 1<sup>d</sup>) and Fig. 14 illustrate that the activity and selectivity of the catalysts even after several cycles of oxidation did not show any significant alteration. The used catalysts were further characterized by FTIR, XRD and EDX spectral studies. The IR (Fig. 5 and Fig. S2, ESI†) and XRD patterns (Fig. 3) of the recovered catalysts displayed close resemblance with those of the fresh catalysts. Furthermore, the elemental analysis and EDX spectral data of the recovered catalysts showed no significant loss in peroxide content and metal loading compared with the fresh ones. These findings clearly demonstrated that the catalysts are structurally robust and are capable of retaining their activity even after reuse in repeated reaction cycles, notwithstanding the relatively higher temperature employed in the case of alkene oxidation.

It is worthy of note that, keeping in view the environmental aspect, we have strategically refrained from using any additional acid or other hazardous additives in our oxidation procedures, as far as possible. Thus, both types of transformations *viz.*, olefin epoxidation and sulfide oxidation, were carried out at the natural pH of the reaction medium.

The merits of the developed catalytic epoxidation methodology with respect to conversion, selectivity and the reaction conditions employed, in comparison with several other reported heterogeneous catalyst systems for styrene epoxidation, are highlighted in Table 9. However, a precise comparison of the TON or TOF obtained is not possible in the absence of sufficient reported kinetic data. It is significant to note that, except for a few reports,<sup>52</sup> most of the metal catalyzed heterogeneous solventfree epoxidation processes utilized TBHP as an oxidant.<sup>46b,49,53</sup> No report however appears to exist related to styrene epoxidation catalyzed by a Ta based catalyst under solventless conditions. As shown in Table 9, we have come across two reports on Ta catalyzed heterogeneous epoxidation of styrene using MeCN as a solvent.<sup>3b,15b</sup> It is further evident from Table S6 (ESI<sup>+</sup>) that the performance of catalysts 1 and 2 in selective sufoxidation is superior to the activities of other Ta(v) catalysts reported so far.<sup>6b,14a,54</sup>

**2.3.5 Proposed catalytic cycle.** It has already been established by work from several laboratories that epoxidation reactions catalyzed by d<sup>0</sup> transition metal peroxo systems usually follow a common reaction pathway which involves the direct electrophilic transfer of the oxygen atom of the peroxo group to the alkene through a spiro-like transition state in a concerted step.<sup>55</sup> Although Ta(v) peroxo systems still remain relatively unexplored, <sup>6c,7b,15a,56</sup> involvement of a catalytically active Ta( $\eta^2$ -O<sub>2</sub>) intermediate species in olefin epoxidation with related supported Ta catalysts has been proposed previously. <sup>6c,7a,b,15a</sup>

Taking into account the aforementioned observations and on the basis of the findings of the present study, we have proposed a credible catalytic cycle for the selective styrene epoxidation mediated by pTa catalysts **1** and **2**. As shown in Fig. 15, in the first step the transfer of electrophillic oxygen from the diperoxotantalate complex of the catalyst to the substrate occurs to form the corresponding epoxide, with concomitant formation of oxoperoxotantalate intermediate II (reaction (a)). The resulting monoperoxotantalate intermediate after the formation of the epoxide combines with the peroxide of  $H_2O_2$  to regenerate the starting complex (I) leading to

Table 9	The comparison of the activity of p	oTa catalysts <b>1</b> and <b>2</b> with	various heterogeneous	catalysts in the epoxidation of styrene
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Entry	Catalyst	Catalyst amount	Conditions [time, temperature, oxidant, solvent]	Conversion (%)/epoxide selectivity (%)	Ref.
1	$[Ta(O_2)_2(Asn)_2]^-$ -MR	0.002 mmol	6 h, 80 °C, 30% $H_2O_2$ , solvent free	100/99	This work
2	$[Ta(O_2)_2(Arg)_2]^-$ - <b>MR</b>	0.002 mmol	6 h, 80 °C, 30% H <sub>2</sub> O <sub>2</sub> , solvent free	84/97	This work
3	Ta-SiO <sub>2</sub>	0.01 mmol	6 h, 65 °C, 30% H <sub>2</sub> O <sub>2</sub> , CH <sub>3</sub> CN	37/36	3 <i>b</i>
4	DET-Ta-MCM <sub>650</sub>	0.015 mmol	24 h, 70 °C, TBHP, CH <sub>3</sub> CN	73/34	15 <i>b</i>
5	α-ZrP·Fe(III)	0.02 mmol	5 h, 80 °C, TBHP, solvent free	28.8/10.8	46 <i>b</i>
6	MP-MoOO <sub>2</sub>	$1.25 imes 10^{-3} \mathrm{~mmol}$	30 min, 95 °C, TBHP, solvent free	95/80	49
7	$(PW_{11})_2/Al_2O_3$	25 mg	4 h, 80 °C, $O_2$ , solvent free	58/56	52 <i>a</i>
8	SBA15-NH <sub>2</sub> -DAMO-Ni	50 mg	24 h, 60 °C, TBHP, solvent free	85/10.6	53 <i>a</i>
9	MoO(O <sub>2</sub> ) <sub>2</sub> (phox)/Fe <sub>3</sub> O <sub>4</sub>	0.0005 mmol	60 min, 95 °C, TBHP, solvent free	90/38	53 <i>b</i>
10	$[MoO(O_2)_2(phox)]/SBA-15$	0.0005 mmol	60 min, 95 $^{\circ}$ C, TBHP, solvent free	87/30	53 <i>c</i>



a catalytic cycle (reaction (b)). Formation of such an oxoperoxotantalate intermediate during oxygen transfer from a pTa species to a substrate has been documented in the literature.<sup>56</sup>

In the catalytic cycle proposed for sulfide oxidation (Fig. 15), the facile transfer of the peroxo oxygen from the diperxotantalum(v) complex of the catalyst to the organic sulfide to yield the sulfoxide (reaction (c)) is accompanied by simultaneous formation of monoperoxotantalate intermediate II. The original catalyst is regenerated subsequently (reaction (b)) when the monoperoxotantalate complex reacts with hydrogen peroxide. The above catalytic cycle is in line with the mechanisms proposed for several other reported peroxometal catalyzed sulfide oxidation reactions.<sup>18b-d,g,h,j,k,51d,57</sup>

### 3 Experimental

### 3.1 Materials

Acetone, methanol, acetonitrile, ethylacetate, hydrogen peroxide, diethyl ether, sodium hydroxide, potassium dichromate, sulfuric acid (E. Merck, India), sodium thiosulphate petroleum ether (boiling range 60-80 °C) (RANKEM), boric acid, sodium bicarbonate, potassium iodide, silica gel (60-120 mesh) (SRL), L-asparagine (Asn), L-arginine (TCI Chemicals (India) Pvt. Ltd), chloromethylated poly(styrene-divinylbenzene) (2.5 mmol  $g^{-1}$ Cl loading, 2% DVB) (MR), pyridine, tantalum pentoxide, methyl phenyl sulfide (MPS), methyl p-tolylsulfide (MpTS), ethyl phenyl sulfide (EPS), dimethyl sulfide (DMS), dibutylsulfide (DBS), 2-(phenylthio)ethanol (PTE), diphenylsulfide (DPS) and allyl phenyl sulfide (APS) were obtained from the Sigma-Aldrich Chemical Company, Milwaukee, USA. Before functionalization, the resin was pre-treated with aqueous dioxane (50:50 (v/v))followed by washing with methanol and dried under a vacuum at 90 °C for 8 h. Distilled and deionized water was used for solution preparation.

### 3.2 Preparation of amino acid grafted polymers

The functionalization of chloromethylated poly(styrene–divinylbenzene) (**MR**) with amino acids L-asparagine or L-arginine was done by following reported methods with some modifications.<sup>18b,25</sup> Pre-washed **MR** beads (2 g, 5 mmol of Cl) were kept for swelling in 6 mL methanol for 1 h. To the swollen polymer in methanol, an aqueous solution of L-asparagine (0.83 g, 6.25 mmol) or L-arginine (1.08 g, 6.25 mmol) in 20 mL water was added and the resulting mixture was refluxed for 24 h at 90 °C in the presence of pyridine (0.50 mL, 6.25 mmol). The overall molar ratio of Cl:amino acid:pyridine on the basis of the percent replaceable chlorine on the polymer was maintained at approximately 1:1.25:1.25. The reaction mixture was subsequently cooled and allowed to stand for one week with occasional stirring. The incorporation of the amino acid was indicated by a change of colour of the polymer beads from off white to yellow. The amino acid functionalized polymer beads were then filtered and washed repeatedly with hot water until no precipitate of AgCl was observed in the filtrate on treating with AgNO<sub>3</sub>. This was followed by washing with ethanol and the beads of **MRArg** or **MRAsn** obtained were finally dried under a vacuum at 90 °C for 8 h.

# 3.3 Preparation of sodium tetraperoxotantalate $Na_3[Ta(O_2)_4]$ ·H<sub>2</sub>O (pTa)

The Na<sub>3</sub>[Ta(O<sub>2</sub>)<sub>4</sub>]·H<sub>2</sub>O complex was prepared by adopting a reported procedure with slight modifications.<sup>20a,d,58</sup> In a nickel crucible, 1 g of tantalum oxide (Ta<sub>2</sub>O<sub>5</sub>) and 1.6 g of NaOH were fused together at 700 °C. The product obtained was cooled and dissolved in 70 mL of 1 M 30% H<sub>2</sub>O<sub>2</sub> with continuous stirring to get a clear solution. The solution was then filtered and the filtrate was allowed to settle in an ice-bath for 12 h. The tetraperoxotantalate was isolated as a white crystalline solid, which was then dried at room temperature.

# 3.4 Synthesis of supported diperoxotantalum compounds $[Ta(O_2)_2(L)_2]^-$ -MR, [L = asparagine (catalyst 1) or arginine (catalyst 2)]

Sodium tetraperoxotantalate  $Na_3[Ta(O_2)_4]$ ·H<sub>2</sub>O (pTa) (1.0 g, 2.5 mmol) was dissolved in 30% H<sub>2</sub>O<sub>2</sub> (10 mL, 88.49 mmol) at ambient temperature. The pH of the reaction solution was observed to be *ca*. 6. Keeping the temperature below 4 °C, 1 g of **MRAsn** or **MRArg** was added to the solution, which was preswelled in 5 mL ethanol for 1 h. The mixture was constantly stirred for 24 h in an ice bath. After decanting the supernatant liquid, the resulting residue was repeatedly washed with acetone. The products were separated by centrifugation and dried *in vacuo* over concentrated sulfuric acid.

### 3.5 Elemental analysis

A PerkinElmer 2400 series II elemental analyzer was used to determine the C, H, and N amounts of the synthesized compounds. The sodium and tantalum content were estimated by inductively coupled plasma-optical emission spectroscopy (ICP-OES). EDX analysis was also used to determine the composition of the compounds. The peroxide amount in the compounds was measured volumetrically by the iodometric method where a weighed amount of the compound was added to a cold solution of 1.5% boric acid (w/v) in 0.7 M sulfuric acid (100 mL) and titrated with standard sodium thiosulfate solution.<sup>59</sup>

### 3.6 Physical and spectroscopic measurements

The IR spectra of the samples were recorded as KBr pellets using a PerkinElmer spectrum 100 FTIR spectrophotometer. The Raman spectra of the compounds were measured using a EZRaman-N (Enwaveoptronics) that was equipped with a diode laser with an excitation wavelength of 785 nm and a laser maximum output power of 350 mW. The measurement parameters were 10 s exposure time, 5 accumulation, laser power 10% of output power and a 100× objective and the pixel resolution was set to 1.44 cm<sup>-1</sup> per pixel. The diffuse reflectance electron absorption spectra of the compounds were recorded using a Hitachi U-3400 spectrophotometer equipped with a diffuse reflectance accessory with an integrating sphere of 60 mm inner diameter and BaSO<sub>4</sub> was used as the standard. The powder X-ray diffraction (XRD) patterns were recorded on a Rigaku X-ray diffractometer (Miniflax, UK) at a scanning rate of 10 °C min<sup>-1</sup> in the  $2\theta$  range 10–70° with the use of Cu K $\alpha$ (k = 0.154 nm) radiation. XPS measurements were performed on a Thermo Fisher Scientific X-ray photo spectrometer with an Al Ka (monochromatic) X-ray source. The source was operated at 12 kV and  $2 \times 10^{-9}$  mbar is the maintained base pressure in the analysis chamber. The charging of the samples was rectified by setting the binding energy of adventitious carbon (C 1s) at 284.6 eV. Thermogravimetric analysis (TGA) was done on a SHIMADZU TGA-50 system under a N2 atmosphere at a heating rate of 10  $\,^{\circ}\mathrm{C}\,$  min  $^{-1}$  by using an aluminium pan. A JEOL JSM-6390LV scanning electron microscope with an attached energy-dispersive X-ray detector was used to carry out scanning electron microscopy (SEM) and energy-dispersive X-ray analysis of the compound. Scanning was carried out in the 1-20 µM range, and the images were taken at a magnification of 15-20 kV. Data were obtained using INCA software. Standardization of the data analysis is an essential part of the SEM-EDX instrument. The <sup>13</sup>C NMR spectra of the compounds were recorded using a JEOL JNM-ECX400II spectrometer at a carbon frequency of 100.5 MHz using 1024 X-resolution points, number of scans 544, 3.5 ms acquisition time and 5 s relaxation delay. The surface areas were determined by nitrogen adsorption/desorption measurements based on the Brunauer-Emmett-Teller (BET) method at 77.3 K on a standard module NOVA 1000E, Quantachrome Instruments. The pore size and pore volumes were measured by the use of the Barrett-Joyner-Halenda (BJH) model using a NOVA 1000E, Quantachrome Instruments.

Magnetic susceptibilities of the complex were determined by the Gouy method with Hg[Co(NCS)] as the calibrant. The melting points of the products were determined on a Büchi Melting Point B-540. GC analysis was carried out using an Agilent 7890A gas chromatograph (GC/GC-MS) with an FID and a 240 ion trap mass detector.

### 3.7 General procedure for epoxidation of alkenes

The catalytic protocol of epoxidation was as follows: to the reaction mixture of the catalyst (containing 0.0025 mmol of Ta) [catalyst 1 (6.8 mg) or catalyst 2 (7.8 mg)] and styrene (5.0 mmol), 30% H<sub>2</sub>O<sub>2</sub> (1.13 mL, 10 mmol) was added to initiate the reaction at 80 °C under continuous stirring. The molar ratio of Ta:substrate:oxidant was maintained at 1:2000:4000. The progress of the reaction was monitored by HPLC. At 80 °C, the distinct phase separation between the organic and aqueous phases of the reaction mixture nearly disappeared as the organic substrate became partially miscible with aqueous H2O2 and the reaction mixture turned cloudy. To monitor the progress of the reaction, aliquots of the reaction mixture were withdrawn periodically after stopping stirring, which caused the solid catalyst to settle at the bottom of the round-bottomed flask. The product and unreacted substrates in the samples were extracted with ethyl acetate. The extracted samples were analyzed with HPLC to monitor the progress of the reaction. After completion of the reaction, the solid catalyst was separated by filtration and washed with acetone for further use.

The quantitative analysis of styrene and its oxidized products was performed on a Thermo-Scientific Dionex Ultimate 3000 HPLC system equipped with a UV detector. The products were detected at a wavelength of 254 nm and well separated by the use of a reversed phase C18 column ( $250 \times 4.6$  mm). The mobile phase was composed of acetonitrile, methanol and water in a volume ratio of 2:3:5 with a flow rate of 1 mL min<sup>-1</sup> and an injection volume of 20 µL. The substrate and products were identified by using authentic samples. The content of the compounds in the sample was determined directly from interpolation of the calibration curves.

### 3.8 General procedure for oxidation of sulfide to sulfoxides

In a typical reaction, the catalyst (0.005 mmol of Ta) [catalyst 1 (13.5 mg) or catalyst 2 (15.6 mg)] and 5 mL of solvent were taken in a 50 mL two-necked round-bottomed flask. 30% H<sub>2</sub>O<sub>2</sub> (2.26 mL, 20 mmol) was added to the reaction mixture with constant magnetic stirring at room temperature. This was followed by the subsequent addition of the substrate (MPS) (5 mmol) to the mixture. The progress of the reaction was monitored by thin layer chromatography (TLC) and GC. After completion of the reaction, the catalyst was separated out from the reaction mixture by filtration and washed with acetone. The reaction products as well as the unreacted organic substrates were then extracted with diethyl ether and dried over anhydrous Na<sub>2</sub>SO<sub>4</sub> followed by distillation under reduced pressure to eliminate the excess diethyl ether. The products were then purified by column chromatography using ethyl acetate-hexane (1:9) as the solvent system. The obtained products were characterized by using IR and NMR spectral analysis and melting point determination for solid products [Text S2, ESI<sup>†</sup>].

### 3.9 Procedure for regeneration of the catalyst

The recyclability of the catalysts was examined using styrene as the substrate for epoxidation. After completion of the reaction as mentioned under Section 3.7, the heterogeneous catalyst was separated by filtration, washed with acetone and dried *in vacuo*. For the next cycle, the recovered solid catalyst was added to a fresh reaction mixture of styrene (5 mmol) and 30%  $H_2O_2$  (10 mmol) to repeat the experiment under the optimized conditions. The progress of the reaction was monitored by HPLC.

In the case of oxidation of MPS to sulfoxide, the solid catalyst was similarly recovered and was placed in a fresh reaction mixture comprising MeOH (5 mL), MPS (5 mmol) and 30% H<sub>2</sub>O<sub>2</sub> (20 mmol) to carry forward the subsequent cycle under the standardized conditions for sulfide oxidation (Section 3.8). The oxidation reactions were repeated up to five reaction cycles in each case.

## 4 Conclusions

In summary, we have developed new heterogeneous catalysts comprising peroxotantalum(v) complexes immobilized on asparagine and arginine grafted cross-linked chloromethylated poly(styrene-divinylbenzene) resin which satisfactorily catalyzed the epoxidation of olefins with excellent TON and TOF under solvent free condition. To our knowledge, this report is the first to demonstrate the use of peroxotantalate based heterogeneous catalysts for solvent free olefin epoxidation. The versatility of the catalysts is further evident from their ability to facilitate the chemoselective oxidation of a broad range of structurally diverse thioethers to the desired sulfoxides in impressive yield and TOF in methanol at ambient temperature. The catalysts are sufficiently robust to afford easy and successful regeneration with reusability at least up to a minimum of five reaction cycles in all cases without any significant loss in activity or selectivity. A high H<sub>2</sub>O<sub>2</sub> efficiency percentage and ready scalability are additional salient features of the catalytic strategies. Most importantly, being absolutely free from halogenated solvent, co-solvent or co-catalysts or any other hazardous auxiliaries, the presented reaction protocols are clean and eco-compatible. Ease of preparation of the catalysts, commercially available starting materials, and simplicity in the work-up procedure are other synthetically valuable attributes of the catalytic systems, making them potentially attractive for practical applications.

# Conflicts of interest

There are no conflicts to declare.

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