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Solvent responsive self-separation behaviour of Brønsted acidic ionic liquid-polyoxometalate hybrid catalysts on H₂O₂ mediated oxidation of alcohols

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ABSTRACT

Two solvent responsive self-separative ionic liquid-based POM hybrids $[DEDSA]_3[PW_{12}O_{40}]$ and $[DEDSA]_3[PM_{012}O_{40}]$ were prepared by combination of diethyldisulphoammonium chloride [DEDSA]Cl with Keggin phosphotungstic acid and phosphomolybdic acid. Properties like water tolerance, high activity, high thermal stability and reusability in these POM hybrid compounds facilitate a new type of POM based catalysis used for oxidation of organic alcohols using hydrogen peroxide as oxidizing agent. Due to varied solubility of the hybrid with different solvents, the hybrid can effectively catalyze the oxidation reaction in homogenous condition and then can finally switch back to heterogenous system and convert as self-precipitating catalyst on addition of suitable solvent at the end of the reaction, which made the recovery and reuse of the hybrid very convenient. The catalysts are characterized via different analytical and spectroscopic tools like FT-IR, ¹H NMR, ¹³C NMR, ³¹P NMR, TGA, UV-Visible, Powder XRD techniques, Raman etc. It was found that the prepared material was highly acidic, thermally stable in nature and was recycled up to 7 times without much loss of catalytic activity.

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1. Introduction

Oxidation of primary and secondary alcohols to carbonyl compounds are being recognized as fundamental essentials for laboratories, pharmaceuticals and other chemical manufacturing industries due to their vital role in organic synthesis [1–3]. Many conventional CrO3 and K2Cr2O7 based oxidant in acidic medium produce over oxidation product of primary alcohol i.e. -COOH from intermediate aldehyde which remains a problem in addition to stoichiometric amount of oxidants, organic solvents, restriction for acid sensitive substrates, release of toxic reagents and inorganic side products to the environment [4-6]. Accompanied by the above mentioned various environmental issues, efforts have been made to produce reasonable oxidation protocols using environmentally benign oxidants having high active oxygen content and producing water as only byproduct at best [7,8]. Polyoxometalates (POMs) are structurally diverse combination of stable metal-oxygen anionic clusters of early transition metals (e.g. M = Mo, V, Ta, W, Nb) at their higher oxidation states in presence of heteroatoms (e.g. X = P, As, Si, Ge) [9]. The wide variation of composition, shapes, sizes and charge densities provide numerous properties which

led to exploration of these materials in catalysis, medicine, materials science, nanotechnology, molecular magnetism etc. [10–20].

They show excellent multi-electron redox cycles without major change of their structures in homogeneous or heterogeneous phases [21–27]. Moreover, they are less toxic as compared to the chromate-based oxidant. The solubility of POMs in polar solvent increases their activity as redox catalysts for the oxidation of alcohol using H_2O_2 as oxidant in homogeneous phase [11,12,28]. The recyclability limitation of homogeneous POMs was solved through heterogenization of the POMs on inert support with high surface area materials. But these supported catalysts also showed slow reaction rates for aggregation and leaching from the support due to weaker binding interaction between them [16]. Consequently, many organic-inorganic hybrid POMs were designed to effectively deal with the problems faced by the POM catalytic systems with modification of their characteristic structural nature like high thermal stability, Brønsted-acidic sites, rich redox properties have been isolated [24-27].

lonic liquids (ILs) have been used extensively for designing task-specific catalysts, used as reaction media and also functionalized solvent because of their unique physical properties such as wider range of melting points to be in liquid state, high thermal stability, viscous nature, appropriate solvation behavior etc.[29]. The presence of organic cation into the POM framework increases







the porosity of the structure and also modify their polarity through hydrophobic interaction which may work as controlling factor for varied solvent responsive behaviour of the hybrid depending on the nature of organic cation. These modifications of the POM structures may facilitate them as a new type of POM-based catalysts having great potential in heterogeneous catalysis. The variation of organic cations in to the POMs provides an efficient approach to synthesize multifunctional materials based on the nature of organic part in molecular level [30]. Task-specific (TSILs) ionic liquids are an important group of ionic liquids with growing applications in synthesis, catalysis, electrochemistry etc. in which functional groups are covalently tethered to the cation or anion or both the ions [31]. Brønsted acidic ionic liquids were designed by tethering acid groups to the ILs and this type of TSILs along with providing acidic functionality to acid catalyzed reactions also helps in avoiding strong mineral acids with volatile harmful acid vapors [32]. Similarly basic TSILs are also designed and were investigated for various applications [33,34]. Ion-pairing of organic cation with the POM anion generates new type of hydrophobic ionic liquidbased hybrid POMs (IL-POMs) as stable solid acidic material with high melting points that can be utilized as heterogeneous catalyst in suitable solvent [35,36].

Modification of the POMs by incorporation of organic moiety has improved the catalytic activity as well as recovery and reusability related issues. Till date several IL-POM hybrids have been studied for base catalyzed reactions, acid catalyzed reactions, oxidation reactions etc. with unique self- separation properties as catalysts based on additive solvent, temperature variation and other stimuli responsive [35-41]. Chen et al. in 2014 developed mesoporous task specific hybrid catalyst of ionic liquid and polyoxometalate, [TMGHA]_{2.4}H_{0.6}PW by self-assembly of tetramethylguanidinium functionalized with hydroxyl and amino groups ionic liquid cation with Keggin phosphotungstic anion. Presence of hydroxyl and amino groups in IL cations of the catalyst leads to surface wettability property and acted as efficient triphasic catalvst for water-mediated oxidation of alcohols [36]. Hou et al. developed two aprotic *N*-methyl-alkylimidazolium polyoxometalates [HDIm]₂[W₂O₁₁] and [DMIm]₂[W₂O₁₁] as reaction induced self-separation catalysts for olefin epoxidation [39]. The study of Brønsted acidic N-alkylsulfonic acid-based IL-POM hybrids was first conducted by Keshavarz et al. as highly self-separation catalyst for esterification reaction [40]. The use of SO₃H-functionalized imidazolium POM hybrid as alternative heterogeneous catalyst for conc. H_2SO_4 in nitration of aromatics was reported by Saikia et al. [41]. No reports are found for designing of direct N-SO₃H functionalized ammonium based Keggin POMs and their catalytic studies in oxidation of alcohol as solvent-sensitive self-separation catalyst in the presence of sulfonic groups through variation of interactions with different solvents. Therefore, herein we aimed to develop direct N-SO₃H functionalized diethyldisulfoammonium salts of Keggin anions, [DEDSA]₃[PM₁₂O₄₀] of phosphotungstic acid and phosphomolybdic acid (Scheme 1) as solvent-responsive recyclable catalysts for oxidation of alcohols using 30% H_2O_2 as green oxidant at 65 °C after characterization with various analytical techniques.

2. Experimental section

2.1. Materials and methods

The required chemicals were collected from Merck and Tokyo Chemical Industry in pure form. Infrared spectra were recorded on Perkin Elmer MIR/FIR-FTIR spectrophotometer. JEOL ECS 400 MHz spectrophotometer was used to take ${}^{1}H$, ${}^{13}C$ and ${}^{31}P$ nuclear magnetic resonance (NMR) spectra (ppm scale) in DMSO d_6 as solvent. Shimadzu UV 1800 spectrophotometer was utilized to study the Hammett acidity plots of the POM hybrid materials. Thermogravimetric analysis (TGA) was performed on Shimadzu TGA-50. Scanning electron microscopy (SEM) images were acquired from JEOL JSM-6390LVSEM besides energy-dispersive Xray (EDX) images. A RENISHAW BASIS SERIES 514 LASERS with green Argon ion laser was utilized to obtain the Raman analyses. Powder X-ray diffraction (PXRD) patterns were noted using a Rigaku Multiflex instrument using a nickel filtered Cu K (0.15418 nm) radiation source and scintillation counter detector. UV–Visible diffusion reflectance (DRS) spectra were collected using Shimadzu 2450 spectrophotometer. Elemental analyses were carried out on PerkinElmer 20 analyzer. Monitoring of oxidation reaction was done by HPLC method using C_{18} reverse phase column and UV detector at 254 nm. Equal mixture of water and acetonitrile was employed as mobile phase at a flow rate of 1 mL/min. The oxidation products were also analyzed using GC-MS having GC



Scheme 1. Synthesis of [DEDSA]₃PM₁₂O₄₀.

model (7890A), MS model (240 Ion trap) and column (Agilent 19091 J-413 HP-5 30 m \times 320 $\mu m \times$ 0.25 μm).

2.2. Preparation of diethyldisulfoammonium salts of Keggin anions $[DEDSA]_3[PM_{12}O_{40}]$ where M = Mo (VI), W(VI)

The -SO₃H functionalized POM hybrid salt [DEDSA]₃[PM₁₂O₄₀] where M = Mo (VI), W(VI) of diethyldisulfoammonium cation containing polyoxometalate Keggin anion [PMo₁₂O₄₀]³⁻ or $[PW_{12}O_{40}]^{3-}$ were prepared in two steps (Scheme 1). Firstly, the initial ionic liquid diethyl disulfoammonium chloride ([DEDSA]Cl) was prepared by dropwise addition of chlorosulfonic acid (30 mmol) using dropping funnel into a stirring solution of diethylamine (15 mmol) in dry CH₂Cl₂ (15 mL) in a two neck 100 mL round bottom flask at 0 °C for 10 min with continuous stirring [42]. Then it was stirred for one hour at room temperature to get a separate laver of the [DEDSA]Cl in dichloromethane solvent. Repeated washing of the reaction mixture with dry CH_2Cl_2 (3 × 10 mL) and followed by decantation remove most of the soluble impurities in dichloromethane. The crude [DEDSA]Cl was obtained as pure light red yellowish liquid after drying in vacuum oven at 50 °C. The formation of this ionic liquid was confirmed from ¹H NMR and ¹³C NMR (Fig. S1).

In second step, 1 mmol of the heteropolyacid (HPA), $H_3PMo_{12}-O_{40}\cdot nH_2O$ (PMA) or $H_3PW_{12}O_{40}\cdot nH_2O$ (PTA) was dissolved in 20 mL of distilled water at room temperature in a 100 mL round bottom flask by continuous stirring. To the stirred solution of HPA, 3 mmol of [DEDSA]Cl was added dropwise within 5 min. Immediately yellow and white precipitation were observed for [DEDSA]_3[PMo_{12}O_{40}] and [DEDSA]_3[PW_{12}O_{40}] respectively. The reaction was continued to stir for another 12 h to complete the precipitation of IL-POM hybrids in water. The product mixture was centrifuged to obtain the IL-POMs i.e. [DEDSA]_3[PW_{12}O_{40}] and [DEDSA]_3[PMo_{12}O_{40}] as water insoluble solids which were washed 3–4 times with distilled water to get analytically pure product. Then the isolated solid products were dried in vacuum oven at 80 °C for 12 h to get 97–99% yields.

2.3. Procedure for oxidation of alcohols

In a typical experiment, a homogeneous solution of 1 mmol of 1-phenylethanol and 3 mol% of [DEDSA]₃[PW₁₂O₄₀] catalyst in CH₃CN (2 mL) was stirred at 65 °C using 30% H₂O₂ (3 mmol) as oxidant for 2 h in a 100 mL two necked round bottom flask fitted with an air condenser in an oil bath. After completion of the reaction as monitored from thin layer chromatographic technique, the acetonitrile solvent was evaporated under reduced pressure and CH₂-Cl₂ was poured over the remaining product mixture. Catalyst selfprecipitates in CH₂Cl₂ and product being soluble in the CH₂Cl₂ was separated by simple filtration. The catalyst was washed with more amount of the CH_2Cl_2 solvent (2 × 2 mL) followed by distilled water. The spent catalyst was reactivated after drying in vacuum oven at 80 °C for 5 h to make ready for next cycle of the oxidation reaction. The crude product mixture obtained from evaporation of the organic solvent was analyzed by HPLC (Fig. S2) as well as GC-MS to monitor the conversion of the substrates and detection of desired products.

2.4. Procedure for Hammett acidity determination of ionic liquid material

The Hammett acidity determination was done by mixing an equimolar amount of basic indicator 4-nitroaniline (5 mg/L, pKa = 0.99) and the ionic liquid material ([DEDSA]Cl / IL-POM hybrids) in CH₃CN solution [43]. The absorbance values of basic indicator [I] in the acidic solution of ionic liquids reduced with increasing acidity of the ionic liquid systems. The Hammett acidity

function (H₀) was calculated using Eq. (1) by measuring the absorption differences [I]/ [HI]⁺ where, $pK(I)_{aq}$ is the pKa value of the basic indicator.

$$H_0 = pK(I)aq. + log [I]/[HI]^+$$
 (1)

3. Results and discussion

The preparation of diethyldisulfoammonium salts of Keggin anions [DEDSA]₃[PM₁₂O₄₀] where M = Mo (VI), W(VI) were carried out in two step method (Scheme 1) as mentioned in the experimental section. The pure IL-POM hybrid salts were analyzed by different analytical techniques for structural confirmations, thermal stability study and for the Brønsted-acidic natures. The redox properties of the IL-POMs were investigated as solvent responsive selfseparation catalyst for selective oxidation of benzylic alcohol to aldehyde and secondary alcohol to keto compound.

3.1. FT-IR analysis

The existence of Keggin structures of heteopolyanions in the IL-POM hybrids were confirmed by comparing their characteristic peaks with the IR spectra of heteropolyacids in Fig. 1(a) & 1(b). It is well defined that α -Keggin anion is a combination of a [XO₄]



Fig. 1. FT-IR spectra of (a) PMA and $[DEDSA]_3[PMo_{12}O_{40}]$ and (b) PTA and $[DEDSA]_3[PW_{12}O_{40}]$ respectively.

tetrahedron of P or Si and [MO₆] octahedra. The [MO₆] octahedral units are edge shared into four $C_{3\nu}$ [M₃O₁₃] groups and are connected to the three-fold axes of the central [XO₄] tetrahedron. The metal atoms are situated at the centres of distorted C_s octahedra with one terminal M-Ot bond. The M-O4c bonds attributes four-coordinate oxygen atoms that connects 3 units of [MO₆] and $[XO_4]$ unit. The $M{-}O_{2c1}$ bonds and $Mo{-}O_{2c2}$ bonds attributes two-coordinate oxygen atoms in which the M-O_{2c1} bonds connects the $[MO_6]$ octahedra into $[M_3O_{13}]$ groups whereas the $M-O_{2c2}$ bonds connect the $[M_3O_{13}]$ units together [44]. Herein, both the POM hybrids displayed peaks correspond to P-O bending (593 cm⁻¹), asymmetric stretch of M–O_{2c2}–M bonds involving edge sharing MO₆ octahedra (714–810 cm⁻¹), asymmetric stretch of M–O_{2c2}–M bonds of corner MO₆ octahedra (866–898 cm⁻¹), asymmetric $M-O_t$ stretch (960–990 cm⁻¹), asymmetric P–O stretch (1049–1097 cm⁻¹) and bending vibrations of water molecules in the secondary structures of the Keggin species (1623-1628 cm⁻¹). The tethering of -SO₃H groups to the diethyldisulfoammonium cation can be attributed from antisymmetric S-O stretch (1147–1166 cm⁻¹), overlapping bands of symmetric S–O stretch with the asymmetric P-O stretch and N-S stretch with the asymmetric stretch of M-O_{2c2}-M bonds of corner MO₆ octahedra were observed. Very weak band of C—N stretch for aliphatic amine at around (1020–1250 cm⁻¹) was observed. The two ethyl groups directly attached to the ammonium cation also showed C—H rocking (1350–1392 cm⁻¹), C—H bending (1450–1470 cm⁻¹) and C—H stretching vibrations (2844, 2943 & 3091–3109 cm⁻¹) in the respective IR spectra of the IL-POMs [40,44–47].

A weak intensity broad band at 3433 cm⁻¹ compared to the heteropolyacids indicates minimum amount of strongly H-bonded water molecules in rigid framework of phosphomolybdate anion and phosphotungstate anion along with –OH bond of sulfonic groups. The reduction in broadening of the O–H band above 3000 cm⁻¹ in the POM hybrids justifies the presence of smaller hydration sphere around the heteropolyanion environment which is also observed in case of deshielding in the resonance peaks in the respective ³¹P NMR spectra of the hybrids [48].

3.2. NMR analysis

Proton NMR analysis of the $[DEDSA]_3[PMo_{12}O_{40}]$ and $[DEDSA]_3-PW_{12}O_{40}$ in DMSO d_6 displayed two $-CH_3$ groups as triplet at 1.12 ppm, two methylene groups as quartet at 2.87 ppm and one broad singlet for two $-SO_3H$ protons at 8.14–8.15 ppm (Fig. 2).



Fig. 2. ¹H NMR spectra of (a) [DEDSA]₃[PMo₁₂O₄₀] and (b) [DEDSA]₃[PW₁₂O₄₀].

The ¹³C NMR of these POM hybrids showed two peaks at 41.83– 42.1 ppm and 11.6 ppm corresponding to ethyl groups of ammonium cation (Fig. S3). The ³¹P NMR spectrum of [DEDSA]₃[PMo₁₂-O₄₀] hybrid salt expressed one peak at -3.65 ppm (Fig. 3(a)) which was observed in higher frequency region compared to -3.51 ppm peak of the phosphomolybdic acid (Fig. S4(a)). In case of [DEDSA]₃PW₁₂O₄₀ there is similar kind of frequency shift of the hybrid to -15.15 ppm is observed (Fig. 3(b)) whereas a single peak appeared at -14.72 for the phosphotungstic acid (Fig. S4 (b)) indicating strong ionic interaction between the organic cation and the Keggin anion. The shift in the resonance peaks in ³¹P indicates dehydration in the IL-POM hybrids which ascribes the presence of smaller hydration sphere in the polyanion environment noticed for dynamic dehydration equilibrium [49,50].

3.3. TGA analysis

Thermogravimetric analysis (TGA) showed absence of physisorbed water (Fig. 4) for the two IL-POM hybrid [DEDSA]₃[PM₁₂- O_{40}] samples up to 100 °C as compared to approximately 12% loss of the physisorbed water in case of the precursor [DEDSA]Cl ionic liquid. The chloride based ionic liquid expressed another



Fig. 4. TGA curves of $[DEDSA]_3[PW_{12}O_{40}]$, $[DEDSA]_3[PMo_{12}O_{40}]$, [DEDSA]CI, H_3 - $PMo_{12}O_{40}$, H_2O and $H_3PW_{12}O_{40}$, H_2O .

degradation at 250 °C which can be expected for stepwise removal of the two $-SO_3H$ group of the diethyldisulphoammonium moiety. The TGA pattern of $[DEDSA]_3[PMo_{12}O_{40}]$ displayed its thermal



Fig. 3. ³¹P NMR spectra of (a) [DEDSA]₃[PMo₁₂O₄₀] and (b) [DEDSA]₃[PW₁₂O₄₀].

stability till 330 °C, whereas it was observed up to 440 °C for the [DEDSA]₃[PW₁₂O₄₀] with residue of the Keggin anions [51]. The least amount of physisorbed water in the POM hybrids can also be evidenced from the respective FT-IR spectra and ³¹P NMR. Although the amount of cation can also be derived from the TGA curves from single step decomposition between 430 °C and 600 °C of the hybrid samples, but in both cases the aproximate % mass loss of three [DEDSA] cations are slightly 6–7% lower than the actual stoichiometric amount i.e. 19% for the [DEDSA]₃[PW₁₂-O₄₀] and 27% for the [DEDSA]₃[PMo₁₂O₄₀]. This can be attributed for encapsulation of some fragments of the organic cationic part with the Keggin anions through strong H-bonding interaction under the degradation temperature.

3.4. Powder XRD analysis

The powder XRD patterns of both the POM-hybrid samples confirmed the presence of Keggin structures of $[PMo_{12}O_{40}]^{3-}$ and $[PW_{12}O_{40}]^{3-}$ in Fig. 5(a) and Fig. 5(b). Typical sharp diffraction peaks of the H₃PMo_{12}O_{40} \cdot nH_2O are observed at 6.80° and 26.59° [Fig. 5(a)]. In case of $[DEDSA]_3[PMo_{12}O_{40}]$, additional small intensity peaks at papeared at around 7–7.75° along with one sharp intesity peak at 6.80, while the other prominent peak of H₃PMo_{12}O_{40} \cdot nH_2O at 26.59° almost disappeared for the hybrid [Fig. 5(a)]. The existence of Keggin structures in $[DEDSA]_3[PW_{12-}O_{40}]$ [Fig. 5(b)] can be attributed from the appearance of character-



Fig. 5. Powder XRD analysis patterns of (a) [DEDSA]_3[PMo_{12}O_{40}] and $H_3PMo_{12}O_{40}$ - nH_2O (b) [DEDSA]_3 [PW_{12}O_{40}] and $H_3PW_{12}O_{40}$ nH_2O .

istic sharp intense peak at 6.78° of the phosphotungstic acid in addition to small intensity peak at $2\Theta = 7.05^{\circ}$ like the hybrid of [DEDSA]₃[PMo₁₂O₄₀]. However, intense peak at 8.55° and 18.46° observed in the H₃PW₁₂O₄₀·nH₂O reduced drastically in [DEDSA]₃[-PW₁₂O₄₀]. In this hybrid, new peaks are found with lower intensity within 2Θ values of 11° - 17° . The disappearance of some sharp peaks and appearance of new peaks in the IL-POM hybrids as compared to their parent acids can be expected from reorganization of crystal structures of the heteropolyacids in the IL-POM hybrids in presence of large organic cation involving self assembly of the Keggin anions and the organic cations via electrostatic force, hydrogen bonding etc [48,52,53].

3.5. Raman analysis

Raman spectra of the hybrids in Fig. 6(a) and (b) showed resemblance of characteristic bands of the Keggin anions $[PMo_{12}O_{40}]^{3-}$ and $[PW_{12}O_{40}]^{3-}$ observed from Bridgeman's assignments [44,54]. A very sharp-edged peak at 992 cm⁻¹ for the phosphomolybdate hybrid is observed for symmetric stretch of Mo-O_t bond coupled asymmetrically to P–O stretching motion along with merging of asymmetric stretch of Mo-O_t bond around 970 cm⁻¹. Another peak at 884 cm⁻¹ is assigned for asymmetric stretch of Mo-O_{2c2}-Mo bonds. Combined stretching and bending vibrations of Mo-O_{2c1}-



Fig. 6. Raman spectra of (a) [DEDSA]₃[PMo₁₂O₄₀] and (b) [DEDSA]₃[PW₁₂O₄₀].

Mo, Mo-O_{2c2}-Mo and O—P—O bonds could be attributed to medium intensity broad shoulder at 605 cm^{-1} . The small intensity sharp peak at 246 cm⁻¹ is accounted for overlapping symmetric stretch of Mo-O_{4c} and bending of the intra ligand Mo-O_{2c2}-O bond. Remaining few very weak Raman bands are related to complex Raman modes of the polyoxometalate anion.

Similarly, in case of the [DEDSA]₃[PW₁₂O₄₀], a very sharp band at 1002 cm⁻¹ is assigned to the symmetric stretch of terminal W-O_t bond. The medium intense band at 910 cm⁻¹ is observed for asymmetric stretch of W-O_{2c2}-W bond. A very weak intensity peaks is observed at 664 cm⁻¹ which could be considered for combined stretching and bending vibrations of W-O_{2c1}-W and W-O_{2c2}-W and O-P-O bonds. The weak band at 226 cm⁻¹ could be allotted for W-O_{4c} stretching and W-O_{2c2}-O bending vibrations.

3.6. UV-Vis diffuse reflectance spectra

The UV–Vis diffuse reflectance spectra of the IL-POM hybrids and the HPAs are represented in Fig. 7(a) & (b). The retention of Keggin structures $[PM_{12}O_{40}]^{3-}$ (M = W or Mo) within the hybrid compounds can be supported from their identical UV–Vis DRS absorption patterns against the respective HPAs. The weak inten-





Fig. 7. UV -Vis DRS of (a) [DEDSA]₃[PMo₁₂O₄₀] and (b) [DEDSA]₃[PW₁₂O₄₀].

sity peaks of phosphotungstate Keggin anion at 259, 347 and 402 nm expressed oxygen to metal charge transfer transition (LMCT) for non-reduced form of the HPA Keggin anion [55], Fig. 7(b). Similarly, for the Keggin anion of the phosphomolybdic acid displayed the weaker LMCT transitions at 218, 347 and 455 nm in Fig. 7(a) [56]. As compared to the HPAs, the Keggin anions of the POM-hybrid samples shifted the position of LMCT transitions to shorter wavelength which indirectly reflect the existence of strong ionic interaction between the constituent ion-pairs [56] and also further observed in the Hammett acidity order. For example, the highest absorption peak of the HPA of phosphotungstate anion shifted from 402 nm to 339 nm in the [DEDSA]₃[PW₁₂O₄₀], hybrid. Likely, with the [DEDSA]₃[PMo₁₂O₄₀], it was shifted to 396 nm from 455 nm.

3.7. SEM analysis

The surface morphology of the hybrid salts $[DEDSA]_3[PMo_{12}O_{40}]$ and $[DEDSA]_3[PW_{12}O_{40}]$ were studied in SEM images at the same magnification in Fig. 8. The SEM topography reveals micrometer sized irregular agglomeration through extensive secondary interactions of intermolecular H-bonds of the two $-SO_3H$ functionality of the ammonium cation with the oxygen atoms of Keggin anions. The fluffy like clustering of aggregates on the surface of $[DEDSA]_3[-PMo_{12}O_{40}]$ will reduce the number of acidic sites on its surface as compared to the smaller size distribution of aggregates in case of





Fig. 8. SEM images of (a) [DEDSA]₃[PMo₁₂O₄₀] and (b) [DEDSA]₃[PW₁₂O₄₀].

the $[DEDSA]_3[PW_{12}O_{40}]$ which was further confirmed by the Hammett acidity study (Fig. 10). The exact reason for differences in the sizes of aggregates are unknown and it is beyond the scope of this study.

3.8. EDX analysis

Energy Dispersive X-ray (EDX) spectrum of the [DEDSA]₃[- $PMo_{12}O_{40}$] in Fig. 9(a) confirmed C, N, O, P, Mo and S as the constituent elements of the hybrid compound, whereas the spectrum of [DEDSA]₃[$PW_{12}O_{40}$] in Fig. 9(b) displayed all the peaks of constituent elements except phosphorus. It can be accounted for low abundance of this element in surface of the Keggin structured anion as compared to high abundances of W and O elements. At the same, the presence of P in the phosphotungstate Keggin anion can be confirmed from the ³¹P NMR spectrum of [DEDSA]₃[$PW_{12}O_{40}$], Fig. 3(b).

3.9. Hammett acidity determination using UV-Visible spectrometry

The Brønsted acidities of [DEDSA]Cl and the IL-POM hybrid salts i.e. $[DEDSA]_3[PMo_{12}O_{40}]$ and $[DEDSA]_3[PW_{12}O_{40}]$ were evaluated as a function of the Hammett acidity (H₀) values as per standard method by UV-visible spectrophotometer using 4-nitroaniline as basic indicator in acetonitrile (Table S1 & Fig. 10) [43]. Their acidi-



Fig. 10. Hammett acidity plot of $[DEDSA]_3[PM_{012}O_{40}]$ and $[DEDSA]_3[PW_{12}O_{40}]$ with respect to parent ionic liquid [DEDSA]CI.

ties can be arranged in descending order depending on ionic strength of the constituent ion-pairs as follows: [DEDSA] $[PW_{12}O_{40}] > [DEDSA]_3[PM_{012}O_{40}] > [DEDSA]Cl$. The greater ionic



Fig. 9. EDX patterns of (a) [DEDSA]₃[PMo₁₂O₄₀] and (b) [DEDSA]₃[PW₁₂O₄₀].

strength between the ammonium cation with the Keggin anions made both POM hybrids more Brønsted acidic than the [DEDSA] Cl involving weaker ionic strength of the chloride anion. Between the two POM hybrids, the presence of higher number of acidic sites with the phosphotungstate hybrid can be described because of minimum sizes of aggregates as evidenced from the SEM image, Fig. 8(b). Similarly, for the phosphomolybdate hybrid, the bigger size clusters exposed minimum number of the acidic sites in the SEM image, Fig. 8(a).

3.10. Catalytic activity

3.10.1. Optimization of reaction condition

To study the redox properties of POM hybrid catalysts, initially we optimized the amount of [DEDSA]₃[PW₁₂O₄₀] by taking 0.5, 1, 2 and 3 mol% of the catalyst for oxidation (Scheme 2) of 1-phenylethanol (1 mmol) in CH₃CN (2 mL) using 30% H₂O₂ (3 mmol) at different temperatures (0 °C, 25 °C, 45 °C, 65 °C, 82 °C) for the specified reaction time as included in Table 1 (entries 1–8). Excellent catalytic activity was observed with 3 mol% of the [DEDSA]₃[PW₁₂-O₄₀] at 65 °C for 2 h to produce 98% yield of acetophenone (Table 1,



Scheme 2. Model reaction for oxidation of alcohol.

Table 1

Study of temperature effects and catalyst amount for the model reaction.

entry 4). So, this amount of catalyst was taken as the standard amount to study the effect of solvents for the model reaction in Table 2. Using the same amount of [DEDSA]₃[PMo₁₂O₄₀] catalyst, the product yield was seen to decrease at 65 °C (Table 1, entry 9). As the amount of this catalyst was increased to 3.5 mol%, the yield of acetophenone increased satisfactorily (Table 1, entry 10). It was also observed that negligible conversion of alcohol occurred in absence of catalyst using 30% H₂O₂ (3 mmol) at 65 °C in acetonitrile (Table 1, entry 11). The redox properties of both of these POM hybrid catalysts were observed to be slightly different with respect to the catalyst amount which was better for the [DEDSA]₃[PW₁₂-O₄₀] catalyst (Table 1, entry 4). This can be attributed for varied coordination abilities of Mo(VI) and W(VI) cations and also different metal-oxygen bond order in their respective in situ generated active species peroxophosphotungstate $\{PO_4[WO(O_2)_2]_4\}^{3-}$ and peroxophophomolybdate $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ as proposed in Scheme 3 for catalytic oxidation of alcohol involving hydrogen peroxide as oxidant [57]. During the oxidation process, the reaction intermediate of alcohol with $\{PO_4[MoO(O_2)_2]_4\}^{3-}$ will be more stable with refilling of electrons in three vacant orbitals 4f, 4d, and 5 s of the Mo species as compared to the intermediate of $\{PO_4[WO(O_2)_2]_4\}^{3-1}$ involving two vacant orbitals, 5d and 6s of the W cation. When the temperature was increased from 65 °C to 82 °C, the oxidation of alcohol was completed within 1.5 h with lowering of percentage yield of acetophenone through formation of byproduct that can be attributed for formation of over oxidized product at 82 °C involving H_2O_2 as oxidant (Table 1, entry 5).

3.10.2. Effect of solvent study

Solvent study was conducted by performing the oxidation of 1phenylethanol in polar solvent including H₂O, MeOH, CH₃CN, EtOAc at 65 °C and in non-polar solvent like CH₂Cl₂, hexane in reflux temperature with the optimized amount of [DEDSA]₃[PW₁₂-O₄₀] catalyst for 2–8 h (Table 2). The results in Table 2 expressed solvent dependence catalytic activity of the POM hybrid with var-

Entry	Reaction Temperature (°C)	Time(h)	Catalyst amount ^[a] (mol%)	Yield % ^[b]
1.	0	8	3	0
2.	25	8	3	0
3.	45	6	3	58
4.	65	2	3	98
5.	82	1.5	3	82
6.	65	2	0.5	16
7.	65	2	1	38
8.	65	2	2	70
9.	65	2.5	3	88
10.	65	2.5	3.5	97.5
11.	65	8	0	<1

^[a] Reaction conditions: (i) using [DEDSA]₃[PW₁₂O₄₀] catalyst: 1-phenylethanol (1 mmol), 30% H₂O₂ (3 mmol), CH₃CN (2 mL) (entries 1–8); (ii) using [DEDSA]₃[PMo₁₂O₄₀] catalyst (entries 9,10); (iii) without catalyst (entry 11).

^[b] Yield % of acetophenone based on GC analysis.

Table 2

Study of solvent effects for the model reaction using $[\mbox{DEDSA}]_3[\mbox{PW}_{12}\mbox{O}_{40}]$ catalyst.

Entry	Solvent	Time (h)	Temperature ^[a] °C	Yield% ^{[a],[b]}
1.	H ₂ O	8	65	45
2.	CH ₃ OH	5	65	78
3.	CH ₃ CN	2	65	98
4.	CH ₂ Cl ₂	8	39	10
5.	n-Hexane	8	68	8
6.	Solvent-free	3	65	60
7.	Ethyl acetate	3	65	66

^[a] Reaction conditions: 1-phenylethanol (1 mmol), 30% H₂O₂ (3 mmol), [DEDSA]₃PW₁₂O₄₀ (3 mol%) catalyst, CH₃CN (2 mL).

^[b] Yield % based on starting substrates in GC analysis.

ied yields of oxidized product which were observed to proceed through either homogeneous or heterogeneous catalytic phases in reaction media. The catalyst was seen to be soluble in MeOH, CH₃CN as polar solvents (Table 2, entries 2, 3) except water making the reaction as homogenous catalysis and the percentage yield of products were raised to higher levels. At the same time, the insolubility of catalyst in H₂O, CH₂Cl₂ and *n*-hexane converts the reaction as heterogenous catalysis and pulling down the percentage yields (Table 2, entries 1, 4, 5). In case of ethyl acetate solvent, the catalyst was found to be sparingly soluble in the reaction medium making the reaction system non homogenous in nature that may be accounted for moderate yield of the product (Table 2, entry 7). The self-precipitation of the $[DEDSA]_3[PW_{12}O_{40}]$ catalyst from the reaction mixture was done by pouring CH₂Cl₂ solvent in the crude product mixture of oxidation obtained Fig. 11(a) after evaporation of the homogeneous solution of reaction in acetonitrile under reduced pressure. The catalyst was recovered and reused after filtration of the dichloromethane solution of oxidation product by keeping in vacuum oven for 5 h at 80 °C. The other polyoxometalate catalyst [DEDSA]₃[PMo₁₂O₄₀] also displayed similar solubility behavior with these solvents which was represented in Fig. 11(b) for the model reaction in acetonitrile. The solvent dependence behavior of the IL-POM hybrid towards polar and non-polar solvent can be considered as a combined outcome of secondary interactions including H-bonding, ion-dipole interactions etc. for each ionic component of the POM with the solvent molecules. The inability of water to solubilize the catalyst can be expected for insufficient H-bonding interaction with the water molecules in presence of two hydrophobic ethyl groups tethered to the ammonium cation of hybrid salt. This factor may become a preferential condition for self-aggregation of the POM hybrid in water through intermolecular H-bonding interactions involving the POM anion and -SO₃H groups of the ammonium cation of the hybrid material. The non-polar solvents like dichloromethane, hexane etc. are favorable for self-aggregation of the POM hybrid. In MeOH and CH₃CN, each of the ionic component of POM hybrid can make sufficient intermolecular H-bonding as well as iondipole interactions with the solvent molecules in presence of slight amount of miscible water which may increase the solubility of the catalyst.

3.10.3. Substrate scope study

The substrate scope study of oxidation reaction was investigated in acetonitrile solution for different substituted benzyl alcohol or cyclic/acyclic secondary alcohol under the optimized condition using [DEDSA]₃[PW₁₂O₄₀] as catalyst (Table 3). The rate of oxidation was found to be relatively high with 3 mol% of the cat-

alyst in case of *p*-methoxy benzyl alcohol and *p*-hydroxy benzyl alcohol (Table 3, entries 4,8) because of strong mesomeric effect as compared to p-chloro benzyl alcohol (Table 3, entry 6). The electron donating substituents in benzyl alcohol expressed excellent yields (Table 3, entry 3) while the substrates with electron withdrawing group showed relatively low reactivity (Table 3, entries 5, 6) as observed from GC analysis. The % yield of oxidised product of p-chloro benzyl alcohol was increased to some extent after increasing the catalyst amount up to 4 mol% (Table 3, entry 7) within 6.5 h reaction at 65 °C in CH₃CN. Surprisingly, the optimized amount of catalyst did not work with cyclohexanol even after increasing the catalyst amount upto 4 mol % (Table 3, entry 9) at the temperature of 65 °C. Acyclic 2° alcohols like 1-phenylethanol and *p*-chloro-1 phenylethanol proceded efficiently for 2–3 h reaction with varied amount of the catalyst (Table 3, entries 1, 11). In case of oxidation of 4-phenyl-1-buten-4-ol, a rearranged α , β unsaturated keto compound was formed after shifting of double bond position without oxidation (Table 3, entry 10). No carbonyl products were obtained under the optimized condition for oxidation of primary alcohol other than benzylic alcohol (Table 3, entry 12).

3.10.4. Plausible reaction mechanism

The mechanism (Scheme 3) demonstrates that the Keggin polyanion in the IL-POM hybrids gets degraded in presence of H_2O_2 to an active metal peroxo intermediate $\{PO_4[MO(O_2)_2]_4\}^3$, which is found to be responsible for the oxidation reaction [7,58,59]. This was further evidenced from respective IR spectrum of peroxo intermediate isolated after treatment of the [DEDSA]₃-PW₁₂O₄₀ with H_2O_2 solution at room temperature (Fig. S5). The spectrum displayed peaks at 857 cm⁻¹ for v(O-O) vibration, 555 cm⁻¹ for symmetric metal-oxygen (W-O₂) stretching frequency and 677 cm⁻¹ for asymmetric (W-O₂) stretching frequency which also proved the involvement of peroxophosphometalate intermediate in the oxidation reaction [60,61].

3.10.5. Recyclability of catalyst

The catalytic recyclability was studied by taking 3 mmol of 1phenylethanol as model substrate with the optimized amount of [DEDSA]₃PW₁₂O₄₀ catalyst for 2 h reaction in CH₃CN at 65 °C. The catalyst was precipitated out from the homogeneous solution of acetonitrile through addition of dry CH₂Cl₂ which is insoluble in CH₂Cl₂. The POM catalyst was then washed with hexane and then reactivated in vacuum oven at 80 °C for 5 h for next catalytic run. Fig. 12 displays reusability profile of the spent catalyst for seven consecutive cycles. Similar catalytic activity with each cycle was observed till third run with modest decrease in yield after the



Fig. 11. Photograph of (a) [DEDSA]₃[PW₁₂O₄₀] and (b) [DEDSA]₃[PMo₁₂O₄₀] switching from homogenous reaction medium in left testube to heterogenous one by self-precipitating in testube kept in right after evaporation of acetonitrile solvent and pouring dry CH₂Cl₂ afterwards.

 Table 3

 Substrate scope for oxidation of alcohols using IL-POM hybrid.

Entry	Substrate	Product	Time (h)	Yield (%) ^[c]
1. ^[a]	OH	o 	2	98
2. ^[a]	HO	H C HO O	6	88.5(2b)9.5 (2c)
3. ^[a]		H O	2	92.5
4. ^[a]		H Jo 3b	1	98.5
5. ^[a]			6	79.4
c [a]	NO ₂	NO ₂	65	540
b. ⁽¹⁾	HO	H	6.5	54.9
7 [b]	CI 64		65	60
7.	HO	HUU	0.5	00
	\bigcup			
	CI Ta	сі _{7b}		
				(continued on next name)

(continued on next page)

Table 3 (continued)



^[a] Reaction conditions: alcohol (1 mmol), H₂O₂ (3 mmol), [DEDSA]₃PW₁₂O₄₀ (3 mol%), CH₃CN (2 mL), 65 °C.

^[b] Reaction conditions: alcohol (1 mmol), H_2O_2 (3 mmol), [DEDSA]₃PW₁₂O₄₀ (4 mol%), CH₃CN (2 mL), 65 °C.

^[c] GC yields based on starting substrates.



Scheme 3. Mechanism of oxidation of alcohol using $[{\rm DEDSA}]_3 PM_{12}O_{40}$ via peroxo intermediate formation.



Fig. 12. Reusability diagram of the $[DEDSA]_3[PW_{12}O_{40}]$ for the model reaction.



Fig. 13. FT-IR spectra of the fresh [DEDSA]₃[PW₁₂O₄₀] and recycled [DEDSA]₃[-PW12O40] after 7th cycle.

fourth run. The reused catalyst almost retains the similar peaks of FT-IR spectrum compared to the fresh catalyst (Fig. 13) after the 7th cycle.

4. Conclusion

Here in this work we designed and presented two novel solvent-responsive thermally stable -SO₃H functionalized ammonium based polyoxometalate hybrids of phosphomolybdic acid and phosphotungstic acid as solid oxidation catalyst. Due to the presence of -SO₃H group in the cation and its nature of hydrogen bonding with the solvent molecules as well with the anions led to the construction of a solvent responsive catalyst which proved to be of great ease while separating catalyst from the reaction medium and also this property helped in switching between homogenous and heterogenous reaction systems. It was used as an efficient catalyst for selective oxidation of substituted benzylic alcohol to aldehydes and acyclic secondary alcohol to keto compounds using hydrogen peroxide as a green oxidant. The catalyst was inactive for oxidation of cyclic secondary alcohol. It also acted as chemoselective oxidant for oxidation of secondary alcohol containing double bond to keto compound with rearrangement of the double bond in α , β position with respect to the carbonyl group. Because of the high thermal stability, high catalytic activity and ease in recovery and reuse enhances this method to be an environment friendly and simpler way for oxidation of alcohols to aldehydes and ketones.

CRediT authorship contribution statement

Niharika Kashyap: Investigation, Methodology. Sukanya Das: Visualization. Ruli Borah: Conceptualization, Supervision.

Declaration of Competing Interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

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Appendix A. Supplementary data

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