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Mesostructure organic-inorganic hybrid ionic liquids based on heteropoly acids: Effect of linkage on the molecular structure and catalytic activity

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Ezzat Rafiee, Department of Inorganic Chemistry, Faculty of Chemistry, Razi University. Kermanshah, 67149, Iran. Email: ezzat_rafiee@yahoo.com; e.rafiei@razi.ac.ir The new inorganic–organic hybrids based on SO_3H -functionalized ionic liquids (ILs) and Keggin-type heteropoly acids $(H_3PW_{12}O_{40}, H_3PM_{012}O_{40}, and H_4SiW_{12}O_{40}; HPAs)$ are prepared and characterized by FT-IR, NMR, XRD, CV, SEM/EDX, ICP-OES, BJH and UV. Different molecular structures according to the different inorganic part were also proved. Potentiometric titration showed a good relationship between catalytic activity and acidity of the catalysts. Electrochemical aspects showed electron transfer ability of the compounds. For understanding catalytic activities of the HPA-IL hybrids in N-formylation reaction, effect of catalyst composition, substrate, and reaction conditions were studied. The best SO_3H -functionalized ionic liquid catalyst was readily recovered and reused for four runs. Easy preparation of the catalyst, simple and easy workup, mild reaction conditions, low cost, excellent yields and short reaction times are the key features of this work.

KEYWORDS

heterogeneous catalyst, Heteropoly acid, mesoporous material, molecular structure, organicinorganic hybrid materials

1 | INTRODUCTION

Hybrid materials are at the interface of the organic and inorganic domains. These materials offer exceptional opportunities not only to combine the important properties from both material domains but to create completely new compositions with really unique properties. Hence, due to these properties of the organic–inorganic hybrids, special attention is paid to their application in catalysis, more precisely biphasic and heterogeneous catalysis.^[1,2]

Ionic liquids (ILs) exhibit fascinating range of properties during the course of the last two decades which include high thermal and chemical stability, un-flammability, suitable solvation behaviors and un-volatility.^[3] Some recent studies have reported that ILs also show outstanding dissolving property for some cellulosic derivatives that insoluble in traditional solvents.^[4–9] Additionally, they are liquid in a wide temperature range and show interesting electrochemical behaviors.^[10] Because of their unique properties, IL has become a unique ecologically favorable access toward modern chemistry to have broad range of potential uses such as synthesis, catalysis, gas absorption, and analysis, etc.^[11,12] A specific category of ILs, namely Brønsted acid functionalized ionic liquids (HILs) with SO₃H-functionalized cations has been reported with high acidic properties and water solubility.^[13,14]

Heteropoly acids (HPAs) constitute a very great and varied class of polyoxometalates (POMs) widely utilized as catalysts in many organic reactions because of their singular structural, acidic and redox properties.^[15–18] However, despite of their main characteristics they apportion common disadvantages such as difficult separation and reutilization of the catalyst, low surface areas $(5-10 \text{ m}^2/\text{g})$ tend to decrease the efficiency of active sites,

unsuitable thermal stability and solubility in polar solvents. These disadvantages can be overcome by dispersal of HPAs on different supports to improve catalytic performances in heterogeneous reaction applications.^[1,19]

HPAs-based hybrid materials are produced by the combination of organic species with HPAs. Recent progresses in ILs investigation reported other paths to obtain organic–inorganic hybrid salts by creation of ionic linkages between an organic IL cation and an inorganic HPA anion. HPAs-based hybrid materials have been widely probed as solid acid catalysts. These materials are anticipated to possess low solubility in organic solvents, high melting point and high mass transfer resistance, and satisfaction as acid catalysts for organic reactions.^[20–23]

Amine formylation to formamides is a key reaction in organic synthesis due to the many usages of formamides as synthetic intermediates.^[24] They have been widely used in the synthesis of pharmaceutically important compounds such as fluoroquinolines, substituted aryl imidazoles, 1,2-dihydroquinolines, nitrogen-bridged heterocycles, isocyanides, formamidines, oxazolidinones. In the Vilsmeier reaction, catalyst was used for allylation and hydrosilylation of carbonyls and also as an important amino protecting group.^[25,26]

In current research, the combination of the cations of SO_3H -functionalized ILs by propane sulfonate with inorganic anionic HPA was used to give composite ILs (HPA-ILs) as effective catalysts. Also, we exhibit the use of special recoverable heterogeneous HPA-ILs for the formylation of amines to produce formamides, under solvent free conditions.

2 | EXPERIMENTAL

2.1 | Material and methods information

All used substances and solvents were bought from Fluka, Aldrich or Merck Company and used without further purification. FT-IR spectra were recorded as KBr pellets using a Shimadzu 470 spectrophotometer. TE-SCAN Scanning electron microscopy (SEM) and energy dispersive X-ray spectroscopy (EDX) were used to examine the morphology and composition of the catalyst. Quantitative bulk elemental composition of the catalyst was evaluated by inductively coupled plasma optical emission spectroscopy (ICP-OES) VARIAN VISTA PRO. X-ray diffraction (XRD) patterns were collected with a diffractometer on Riguka, Japan, RINT 2500 V using Cu-Kα radiation. ¹H NMR spectra data for SO₃H functionalized ILs were recorded by BRUKER 300 MHz AVANCE III. The potential variation was measured with a Metrohm 713 pH meter. The absorption spectra of UV-vis were achieved with T80 double beam UV-vis spectrophotometer (NORDANTEC-GmbH) diode-array spectrometer using quartz cells of 1 cm optical path and the concentration of samples is 0.1 g/l in water. The N₂ adsorption-desorption isotherm and BJH pore diameter distribution were estimated on a Sorptometer Kelvin 1042 using nitrogen adsorption at 77 K. The electrochemical behavior of the catalyst was studied in Dimethyl sulfoxide (DMSO) (0.5 M NaClO₄). A glassy carbon electrode was used as the electrode and Ag/AgCl as the reference electrode. Cyclic voltammograms (CV) were obtained at a scan rate 0.2 V/s and ambient temperature (20 \pm 5 °C). The porosity was measured with sorptometer kelvin 1042 using nitrogen adsorption at 77 K. The selected products of N-formylation were characterized by ¹H NMR using a Bruker Avance 400 MHz NMR spectrometer.

2.2 | Preparation of the catalysts

2.2.1 | Preparation of 4,4'-bis(3sulfopropyl) bipyridinium (bPyPS) and 4,4'-bis(4-sulfobutyl) bipyridinium (bPyBS)

4,4'-bipyridine (1.56 g, 0.01 mol) was solved in 10 ml dimethyl sulfoxide. Then 0.025 mol 1,3-propane sultone (PS) or 1,4-butane sultone (BS) was added slowly within 5 min and this mixture was stirred for 6 hr at 80°C. The reaction mixture was distilled to remove dimethyl sulfoxide, then washed with diethyl ether five times and dried at 100°C for 3 hr. The final products denoted as bPyPS or bPyBS were white powders (Scheme 1).

2.2.2 | Preparation of HPA-ILs

For the synthesis of HPA-IL catalysts, $H_3PW_{12}O_{40}$ (PW), $H_3PMo_{12}O_{40}$ (PMo) and $H_4SiW_{12}O_{40}$ (SiW) are used as HPA. The resulting bPyPS (0.004, 0.004 and 0.0027 mol) was added to an aqueous solution of PW, PMo and SiW (0.0027, 0.0027 and 0.00133 mol in 10 ml H₂O) respectively. The mixture was stirred at room temperature for 24 hr. Water was removed in a vacuum to give the final products (bPyPS)₃(PW)₂, (bPyPS)₃(PMo)₂ and (bPyPS)₂(SiW)₂ denoted as bPyPSPW, bPyPSPMo and bPyPSSiW respectively, which are respectively white, green and white powders. 0.004 mol of bPyBS was added to an aqueous solution of PW (0.0027 mol in 10 ml H₂O) to synthesize bPyBSPW. Mixture was stirred at room temperature for 24 hr. Final white product (bPyBS)₃PW denoted as bPyBSPW was obtained after water removal.



SCHEME 1 Structures of the SO3H-functionalized ILs

2.3 | Acidity measurement

For measurement of the acidity of samples using potentiometric titration, 0.05 g of solid catalyst was suspended in 90 ml of acetonitrile and stirred for 3 hr. Then the suspension was titrated with 0.05 N solution of n-butylamine in acetonitrile. The potential variation was evaluated with a Metrohm 713 pH meter using a double junction electrode.

2.4 | N-formylation reactions under solvent-free conditions

A blend of aniline (1.0 mmol), aq. formic acid (98%, 2.0 mmol), and HPA-ILs (0.020 g) was stirred at room temperature under solvent-free conditions. The progress of the reaction was continuously monitored by Thin-Layer Chromatography (TLC). After the reaction completion, as indicated by TLC tests, the catalyst was recovered with addition of ethyl acetate to the reaction mixture and washed with ethyl acetate. Then the catalyst was dried to be reused in a new N-formylation reaction. The isolated organic phase was washed with a saturated solution of NaHCO₃ and dried over anhydrous Na₂SO₄. The crude product was purified by column chromatography on

silica gel using EtOAc/hexane as eluent. Selected isolated products gave suitable spectral data (¹H NMR) and compared with those reported in literature.^[27,28]

3 | RESULTS AND DISCUSSION

The HPA-IL catalysts were synthesized by two-step reaction (Scheme 1, 2). The zwitterionic-type compounds were prepared through one-step sulfonation, reaction of 4, 4'bipyridine with 1,3-propane sultone or 1,4-butane sultone. The zwitterionic products were analyzed by ¹H NMR (Figure 1). Based on ¹H NMR results no by-product was produced in bPyPS synthesis procedure and present of two type of aromatic hydrogens shows 1,3-propane sultone was connected to each two N atoms in 4, 4'-bipyridine molecule. In these spectra, the peaks of the aliphatic hydrogens of bPyPS were observed in 4.83, 2.97 and 2.47 ppm, related to CH₂-N, CH₂-S and C-CH₂-C respectively (Figure 1a). Nevertheless, in bPyBS product 1,4-butane sultone was connected to only one N atom in 4, 4'-bipyridine molecule (Figure 1b).

The zwitterion acidification was performed by mixing of bPyPS with PW, PMo and SiW as well as bPyBS with PW, which led to the creation of organic–inorganic salts.



SCHEME 2 Preparation of bPyPSPW as an example



FIGURE 1 ¹H NMR spectra of (a) bPyPS and (b) bPyBS



FIGURE 2 FT-IR spectra of (a) bPyPS, (b) PW, (c) bPyPSPW, (d) reused bPyPSPW, (e) bPyBS, (f) bPyBSPW, in left, and (a) bPyPS, (b) PMo, (c) bPyPSPMo, (d) SiW, (e) bPyPSSiW in right

The procedure of synthesis of bPyPSPW was showed in Scheme 2 as an example.

In our investigations, we made HPA-ILs with different HPA and IL parts, and their structural characteristics were studied using FT-IR, UV-vis and XRD techniques. Characteristic peaks of Keggin anions present in the HPA-ILs have been shown in the FT-IR spectra (Figure 2) which are useful to investigate the structural and bonding changes of these compounds. The vibrational bands for $[PMo_{12}O_{40}]^{3-[29]}$ are shown in 1064 cm^{-1} (P-O), 961 cm^{-1} (Mo = O), 871 cm^{-1} (Mo-O_c-Mo) (corner-sharing), and 779 $\rm cm^{-1}$ (Mo-O_e-Mo) (edge sharing). The bands $\rm [SiW_{12}O_{40}]^{4-[30]}$ are placed at 1019 cm⁻¹ (Si-O), 983 cm⁻¹ (W=O), 924 cm⁻¹ (W-O_c-W) (corner-sharing), and 781 cm^{-1} (W-O_e-W) (edge sharing). The typical bands $[PW_{12}O_{40}]^{3-[31]}$ are illustrated in 1080 cm⁻¹ (P-O), 984 cm⁻¹ (W=O), 896 cm⁻¹ (W-O_c-W), and 814 cm^{-1} (W-O_e-W) bands. In the HPA-ILs, the characteristic bands are at the same wavenumbers or with a small shift according to the interaction HPA with IL. Moreover, vibrations at 1036 and 1165 cm⁻¹ can be attribute to stretching mode of sulfonic groups in catalysts and N-C quaternization stretching frequency at 1640 cm ⁻¹. The results exhibit that the amplification and weaken-

ing of the bonds of the HPAs is due to the interaction between the SO_3H -functionalized IL cations and the HPAs (Figure 2).

UV-vis is a very suitable method to study the electronic properties of the metal-center ions. Most of HPAs have characteristic bands in the middle of the range UV-vis. The spectra of HPA-ILs are shown in Figure 3. A distinctive peak of the HPAs in their non-reduced form was depended on ligand to metal charge transfer (LMCT) band that seem in the UV area below 400 nm.^[32-34] Radiance UV light to HPA-ILs causes the electrons to excite from the low-energy electronic levels (O, 2p orbitals) to the high-energy levels (metal, d orbitals). The size of the cluster and counter-cation in HPAs affect their energy of the electronic transitions. The absorption bands at 205 nm (bPyPSPW and bPyPSPMo) and 210 nm (bPyBSPW) related to the $O \rightarrow P$ transition and the $O \rightarrow Si$ transition has the absorbed band at 205 nm (bPyPSSiW). The bands appear at 255 nm for bPyPSPW and bPyBSPW, and 260 nm for bPyPSSiW are owing to the LMCT of $O^{2-} \rightarrow W^{6+}$ in the Keggin units of HPA.^[35-38] The bPyPS and bPyBS cations have an intense and broad absorption band at approximately 260 nm, ascribed to the π - π * transition of the 4, 4'-bipyridine. The results indicate that in four compounds of HPA-ILs Keggin structure of HPAs is preserved in spite of interaction with bPyPS and bPyBS cations.

For more investigation, cyclic voltammetry was used to study electrochemical behavior of HPA-ILs. Figure 4 shows the CV of IL, HPA and HPA-ILs for comparison.



FIGURE 3 UV-Vis spectra of HPA-ILs



FIGURE 4 CV of ILs, HPAs and HPA-ILs (0.03 g) in DMSO (0.5 M NaClO₄), scan rate 0.2 V/s, ambient temperature (20 ± 5°C)

| | Enc Ena | | Potential Shift | | |
|----------|---|--|---------------------------------------|---------------------------|--|
| Catalyst | (V) | (V) | $\Delta E_{pc} (V)^{a}$ | $\Delta E_{pa} (V)^{b}$ | |
| PW | -0.162 -0.732 -1.233 | 0.733 -0.295 -1.203 | | | |
| bPyPSPW | $1.532 \\ -0.184 \\ -0.932 \\ -1.272 \\ -2.190$ | $1.542 \\ 0.464 \\ -0.104 \\ -1.292 \\ -1.921$ | 0.021 0.200 0.039 | 0.269 -0.191 -0.089 | |
| bPyBSPW | -0.843 -1.451 -2.071 -2.361 -2.870 | 0.713 -0.824 -2.550 | 0.111 0.218 | 0.020 -0.379 | |
| РМо | 0.266 0.056 -0.203 -0.662 -1.241 | 1.503 0.366 -0.083 | | - | |
| bPyPSPMo | 1.434 0.177 -0.012 -0.391 -1.040 | 0.316 -0.152 -0.372 -0.751 -1.260 | - 0.089 0.068 0.188 0.201 | - 0.050 0.069 | |
| SiW | $1.372 \\ -0.594 \\ -1.143 \\ -2.041 \\ -2.171$ | 1.332 0.733 -0.404 -0.983 -2.431 | | | |
| bPyPSSiW | 1.382 -0.863 -2.181 | 1.282 0.673 -0.943 | -0.010 0.269 0.140 | 0.050 0.060 0.040 | |
| | -2.321 | -2.401 | 0.150 | -0.030 | |

^aE_{pc} (HPA) - E_{pc} (HPA-IL).

^bE_{pa} (HPA) - E_{pa} (HPA-IL).

The shift in the potential of some redox peak of HPA-ILs, clearly shows the interaction between HPA and IL. The amount of the shifts in different peaks are reported in Table 1. Investigation of CV of bPyPSPW, bPyPSPMo, and bPyPSSiW show that their electrochemical synergistic behavior is suitable and keep the electrochemical property of HPA in the HPA-ILs. In CV of bPyBSPW, some peaks have shifted and some merge.

The XRD patterns of bPyPS, bPyPSPW, bPyPSPMo, bPyPSSiW, bPyBS, bPyBSPW, PW, PMo and SiW were also investigated (Figure 5). XRD patterns of HPA-ILs

demonstrate that the crystalline structure of HPA as the result of interaction with IL converted to non-crystalline structure.^[39]

The acidity of HPAs was affected with formation of HPA-ILs. Potentiometric titration with an organic base was used for acidic properties investigations. Titration curves obtained for different SO₃H-functionalized HPA-ILs are presented in Figure 6. It is considered that the maximum strength of the acid sites is exhibited with the initial electrode potential (E_i) . Value from which the plateau is reached (mmol amine/mmol catalyst) indicates the total number of acid sites (n_a) that are present in the titrated solid.^[40] As shown in Figure 6, all produced HPA-ILs displayed very strong acid sites, $E_i > 100$ mV. Based on Figure 6a, it seems that IL affect the Ei of PW and bPyBS decrease E_i of PW more than bPyPS, although both of bPyBSPW and bPyPSPW are very strong acids $(E_i > 100 \text{ mV})$. According to the titration curves, it was observed that relative acidic strength of bPyPSPW is more than bPyBSPW (Figure 6a), bPyPSPMo and bPyPSSiW (Figure 6b). Strength of acidic sites of produced HPA-ILs is as the following trends: bPyPSPW > bPyPSPMo > bPyPSSiW > bPyBSPW (E_i values for these compounds are 472.5, 301.0, 293.8, and 222.2 mV respectively). As a result, probably bPyPSPW may show higher catalytic activity due to higher acidic strength of this catalyst and the number of acidic sites (n_a) of bPyPSPW is 1.8 that is higher than other HPA-ILs.

More investigations on bPyPSPW have been done. The content of W and S was evaluated quantitatively by ICP-OES, which showed 43.93% and 2.34% respectively. Based on this data, bPyPS to PW molar ratio is 3:2 in this catalyst that corresponded with neutralization of electrical charge and possible molecular formula of [(bPyPS)₃(PW)₂]. Elemental analysis carried out using EDX (Figure 7a) showed the presence of C, N, P, W, O and S. Morphology of bPyPSPW was investigated by SEM (Figure 7b, 7c).

The porous nature of the best catalyst was studied using BJH method. The N_2 adsorption-desorption isotherm and BJH pore diameter distribution are shown in Figure (7d, 7e) Based on the isotherm curve, bPyPSPW is mesoporous with the pore diameter of 25 nm.

3.1 | Investigation of catalytic activity of HPA-ILs in N-formylation reactions

Catalytic activities of synthesized HPA-ILs were studied by N-formylation reaction. The reaction of aniline with formic acid was chosen as a model reaction of Nformylation (Scheme 3).



0 0 -100 -100 -200 -200 -300 -300 0 1 2 0 1 2 mmol amine/ mmol catalyst mmol amine/ mmol catalyst FIGURE 6 Potentiometric titration curves of different HPA-ILs, different ILs and HPAs

In an experiment, this reaction was performed in the lack of HPA-ILs under solvent-free conditions that progress of reaction was 40% (Table 2, entry 1). This reaction was performed in the attendance of bPyPS and bPyBS as catalyst (Table 2, entry 2, 3). Considering to acidity property of SO₃-functional IL (bPyPS) the reaction efficiency was relatively high but it is not suitable as catalyst because of harsh recovery. It should be noted that only 5 wt.% of the bPyPS was recovered. Therefore, organic-inorganic hybrid salts (HPA-ILs) can be used to enhance recycling. Catalytic activity of different HPA-ILs determined that bPyPSPW is the best catalyst among other HPA-ILs [Table 2, entry 4–7].

Based on obtained results, increase of catalysis activity bPyPSPW is proportional to its acidity and number of acidic sites (Figure 8).

Optimum amount of the catalyst was determined by examination of different amounts of the catalyst (Table 3, entry 1–5). The results of Table 3 indicated that optimum amount of bPyPSPW was 0.020 g. Also, the content of used formic acid is very important. The usage of additional amount of formic acid under the same reaction conditions increases time of the reaction and the yield of the product decreases (Table 3, entries 1, 6–8). The suitable amount of formic acid is 2 mmol. To study the influence of the solvents, reactions were carried out in ethyl acetate, acetonitrile, dichloromethane, dimethyl sulfoxide and ethanol (Table 3, entry 9–13). Catalytic performance in solvent system showed very low yield.

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Therefore, 0.020 g of the bPyPSPW and 2 mmol of formic acid were chosen in solvent free conditions for further reactions.

A series of aniline derivatives and formic acid were examined under the optimum conditions and the results are reported in Table 4.

Activity of the recovered catalyst is an important advantage when it is introduced for practical application



FIGURE 7 (a) EDX pattern (b, c) SEM image (d) Nitrogen adsorption-desorption isotherm and (e) BJH plot of bPyPSPW



SCHEME 3 N- formylation of amine in the presence of HPA-ILs.

in catalytic processes. The recycling performance of bPyPSPW was investigated in several runs of N-

formylation reaction in solvent free conditions. At the end of the reaction, bPyPSPW was washed with ethyl acetate, separated by centrifuging and dried under vacuum. bPyPSPW was 90 wt.% recyclable. The yield of the product in model reaction for the first run decreased down to 80% after fourth run (Figure 9).

The reused catalyst was investigated by SEM/EDX (Figure 10a, 10b and 10c). Morphology of the reused

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TABLE 2Investigation of activity of different catalysts in the N-
formylation reaction^a

| Entry | Catalyst | Time (min) | Yield (%) |
|-------|----------|------------|-----------|
| 1 | - | 10 (60) | 40 (40) |
| 2 | bPyPS | 35 | 75 |
| 3 | bPyBS | 35 | 65 |
| 4 | bPyPSPW | 25 | 90 |
| 5 | bPyBSPW | 15 (25) | 65 (65) |
| 6 | bPyPSPMo | 60 | 75 |
| 7 | bPyPSSiW | 60 | 75 |

^aAniline (1 mmol), formic acid (2 mmol), and catalyst (0.02 g) in solvent free conditions at r.t.



FIGURE 8 Yield of the product as a function of catalyst acidity and the number of acidic sites after 25 min

TABLE 3 Optimization of model reaction conditions in the presence of bPyPSPW

| Entry | Catalyst (g) | Solvent | Formic acid (mmol) | Time (min) | Yield (%) |
|-------|-----------------|------------------------------|-----------------------|---------------|--------------|
| 1 | 0.010 | Neat | 2 | 50 | 45 |
| 2 | 0.015 | Neat | 2 | 70 | 78 |
| 3 | 0.020 | Neat | 2 | 25 | 90 |
| 4 | 0.025 | Neat | 2 | 50 | 81 |
| 5 | 0.030 | Neat | 2 | 40 | 83 |
| 6 | 0.020 | Neat | 1 | 60 | 42 |
| 7 | 0.020 | Neat | 3 | 40 | 89 |
| 8 | 0.020 | Neat | 5 | 90 | 82 |
| 9 | 0.020 | EtOH | 2 | 60 | 77 |
| 10 | 0.020 | DMSO | 2 | 60 | 65 |
| 11 | 0.020 | CH_3CN | 2 | 60 | 80 |
| 12 | 0.020 | Ethylacetate | 2 | 25 | 81 |
| 13 | 0.020 | $\mathrm{CH}_2\mathrm{Cl}_2$ | 2 | 25 | 79 |

Aniline (1.0 mmol) and formic acid at room temperature.

TABLE 4 N-formylation of some amines using bPyPSPW ascatalyst^a

| Entry | Substrate | Time (min) | Product ^b | Yield (%) |
|-------|--|---------------|--|--------------|
| 1 | | 25 | NHCHO | 90 |
| 2 | H ₃ C-NH ₂ | 25 | Н ₃ С | 91 |
| 3 | CH ₃ CH ₂ -NH ₂ | 25 | CH ₃ CH ₂ -NHCH | 92 |
| 4 | NH ₂ CH ₂ CH ₃ | 30 | NHCHO CH ₂ CH ₃ | 84 |
| 5 | | 45 | но | 83 |
| 6 | | 40 | СІ | 80 |
| 7 | | 60 | сі МНСНО | 72 |
| 8 | Br-NH2 | 70 | Br-NHCHO | 75 |
| 9 | F-NH ₂ | 70 | F | 76 |
| 10 | O ₂ N-NH ₂ | 160 | 0 ₂ N-NHCHO | 66 |

 $^{\rm a}Aromatic amine (1 mmol), formic acid (2 mmol), and bPyPSPW (0.02 g) in solvent free conditions at r.t.$

 $^{b}Isolated yield; selected products were identified by comparing their <math display="inline">^{1}H$ NMR with those in authentic samples. $^{[27,28]}$



FIGURE 9 Reusability of bPyPSPW in the model reaction after 40 min

bPyPSPW compare with bPyPSPW has more uniform distribution and less agglomeration that was probably due to abrasion in solvent free conditions. Data of EDX revealed the presence of several elements including C, N, P, W, O and S without significant change in weight percent of the elements.

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FIGURE 10 (a, b) SEM image and (c) EDX pattern (d) Potentiometric titration curves of reused bPyPSPW

Moreover, there is no significant change in the FT-IR spectrum (Figure 2d in left). Also, the acidity of reused bPyPSPW was probed by potentiometric titration (Figure 10d). Strength of acidic sites of reused bPyPSPW was decreased toward bPyPSPW (E_i values are 332.5 and 472.5 mV respectively). The reduction in efficiency of reused bPyPSPW can be justified through reduce in acidic strength.

4 | CONCLUSION

In conclusion, we have developed a simple method by reaction between HPAs and SO_3H -functionalized organic cations to produce SO_3H -functionalized HPA-ILs. The materials showed promising catalytic activity for N-formylation reaction in solvent free conditions. The acidity of different SO_3H -functionalized HPA-ILs was probed by potentiometric titration. The results show that bPyPSPW in comparison with other catalysts exhibited excellent catalysis activity for production of formamides. This catalytic reaction was carried out under solvent-free conditions that can be considered as "Green procedure"

due to no damaging volatile solvent is unfastened into the environment. The isolated catalyst was stable under the present reaction conditions, could be reused at least four times with tiny loss of its catalytic activity.

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